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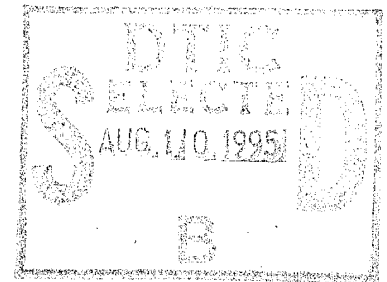
**ASSESSMENT OF OCCUPATIONAL AND
ENVIRONMENTAL HEALTH HAZARDS OF
FIREFIGHTING TRAINING**



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Final Report for July 1991 - October 1991

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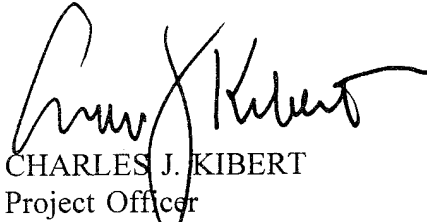
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This technical report has been reviewed and is approved for publication.




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13. ABSTRACT (Maximum 200 words) This study was designed to assess the inhalation hazards to both fire-fighting personnel and the surrounding communities associated with the use of halocarbon-based firefighting agents during training exercises and actual flightline fires. The currently used agent, Halon 1211, was tested as well as two possible replacements, HCFC 123 and perfluoro-hexane. A variety of test methods was used at various locations including the upwind, downwind, and plume zones, generally at breathing height. Volatile organic and inorganic gases were the primary targets along with potentially carcinogenic semivolatile organics including dioxins and furans. Acid gases, including COF ₂ , HF, HCl, and HBr, were found to exceed the immediately Dangerous to life and Health (IDLH) limits in the downwind plume. Total acid gas toxicity was similar for all three agents. High concentrations of the neat agents were also found, especially near ground levels.				
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EXECUTIVE SUMMARY

A. OBJECTIVE

This study was designed to assess the inhalation hazards to firefighting personnel associated with the use of halocarbon-based firefighting agents during training exercises and actual flightline fires. The study also examined possible long-range atmospheric transport and long-term human exposure of the surrounding communities to these firefighting hazards.

B. BACKGROUND

Fire-training exercises are routinely conducted for Air Force personnel at locations throughout the United States. Jet fuel, usually JP-4, is typically combusted in a circular test pit or cement dike, while firefighters are directed to safely and effectively extinguish the blaze. During these exercises, firefighters may be exposed to airborne vapors, aerosols, and gases from the jet fuel, the extinguishing agent, and the combustion products of both, the hazards of which are largely unknown.

The extinguishing agent widely used by the Air Force is Halon 1211. Due to the ozone depletion potential associated with Halon 1211, a replacement agent is currently being sought. Firefighter safety, community exposure, and extinguishing effectiveness, however, are also important considerations for choosing a replacement agent. This study examines the issues of firefighter safety and community exposures, and was funded as part of the U.S. Air Force Halon 1211 Replacement Program.

C. SCOPE

Field tests to assess the firefighter exposure were conducted in two separate phases, a Screening Study and a Main Test. In the Screening Study, a wide variety of sampling methods was used to evaluate the best techniques for the final test matrix. Halon 1211 was used as the extinguishing agent for the Screening Study.

The Main Test, designed from the Screening Study results, examined the effects of halocarbon agents Halon 1211, HCFC 123, and perfluorohexane (PFH) upon a JP-4 fire. An emissions (hazard) comparison was made between the currently used agent, Halon 1211, and the two possible replacements, HCFC 123 and PFH. Following collection of field measurements, atmospheric dispersion models were applied to project the fate and effects of plume components leaving the training site.

D. METHODOLOGY

Sampling and analysis methods used during both the Screening Study and Main Test were based on standard air-sampling techniques modified to fit the firefighter training scenario. Since it was not yet known which methods were most useful, the Screening Study utilized a wide variety of methods. Summa® canisters,

Tenax®/carbon molecular sieve traps, PUF samplers, long-path FTIR and CO monitoring were all performed. Volatiles and semi-volatiles were analyzed by GC/MS, regardless of the sample collection media.

Based on information gathered during the Screening Study, a test matrix for the Main Test was developed. Sampling methods for the Main Test again included Summa® canisters, PUF samplers, and long-path FTIR. Tenax®/carbon molecular sieve traps were replaced with Tenax®/charcoal traps for better collection of highly volatile compounds. CO monitoring was dropped from the Main Test. Length-of-stain tubes were added to the matrix, providing a second technique (besides FTIR) for measurement of acid gases in the plume.

E. TEST DESCRIPTION

Both the Screening Study and the Main Test were performed at the New Mexico Engineering Research Institute (NMERI) test site in Albuquerque, New Mexico. A 75-square foot pool fire of JP-4 was used for the Screening Study, and only Halon 1211 was used as an extinguishing agent. The Screening Study consisted of six test runs with various sampling locations and burning conditions, thus collecting the greatest amount of information with which to design the Main Test matrix.

The Main Test was designed to simulate an aircraft engine and fuel spill fire. This was accomplished by using a 55-gal drum apparatus suspended approximately four feet above the 75-square foot circular fire pit. JP-4 was used as the fuel, and Halon 1211, HCFC 123, and PFH were used as agents. To gain maximum information, the sampling equipment was set up in a variety of locations, including the upwind, downwind, and plume zones, generally at breathing height. A total of ten tests was performed; the three agents were used in three separate runs apiece, plus one background test using only JP-4.

F. RESULTS

The Main Test results provide extensive information for VOCs, semivolatiles, PCDD/PCDFs, halon agent, and acid gas concentrations at upwind, downwind, and plume locations. The greatest firefighting hazard was found by the acid gas detection methods (FTIR and length-of-stain tubes). These methods showed HBr, HCl, and HF at or above Immediately Dangerous to Life and Health (IDLH) levels in the downwind plume, with the exact compounds present depending upon the agent being tested. The FTIR also detected an unknown compound, later identified as carbonyl fluoride, near or above the estimated IDLH levels.

VOC results showed significant, but less than IDLH, levels of benzene, toluene, and halocarbons. Downwind and plume samples showed the highest levels, while the lowest levels were found in the upwind direction. Semivolatile results showed significant, but less than IDLH, levels of JP-4, with insignificant levels of some polynuclear aromatic hydrocarbons (PAHs) and dioxins/furans near detection limits.

The halocarbon samplers, which were arranged in a vertical profile, showed the greatest halocarbon concentrations near the ground, with much lower concentrations at the firefighter's breathing height. This effect was expected due to the greater density of halocarbon agents.

G. CONCLUSIONS

Firefighter exposure to the acid gases, as measured by FTIR and length-of-stain tubes, poses the greatest single threat to site personnel when using any of the three agents. The acid gases were frequently measured at or above IDLH levels. The exact hazards measured at upwind, downwind, and plume locations for each of the three agents are summarized along with other significant conclusions in Section VII.

H. RECOMMENDATIONS

Use of all known halocarbon extinguishing agents must be carefully evaluated due to their universal production of acid gases when applied to a flame or high temperature source. Such agents should only be used by trained personnel who will preferably attack a fire from the upwind direction to minimize their chance of exposure to the plume gases. Other recommendations are summarized in Section VIII and should be reviewed prior to decision-making concerning the use of halocarbon agents.

I. APPLICATION

Data from the Main Test were applied to an air dispersion model to assess community exposure. Downwind dispersion of the plume was modeled using the ISCST Version 09348 model from the U.S. EPA. Worst case meteorology was determined with a PTMAX 49-element windspeed/stability class matrix. Models were run using conservative assumptions and, in some cases, the combined acid gas toxicities exceeded IDLH levels at distances up to 260 meters from the source. Long-term dispersion model results for the maximum exposed individual showed less than 3×10^{-7} cancer risk due to benzene and dioxins/furans.

J. BENEFITS

Results of this study will allow the Air Force to better assess future choices for extinguishing agents while balancing health hazards, community exposure, and ozone depletion potential.

K. TRANSFERABILITY OF TECHNOLOGY

This report will be of interest to the Air Force, communities adjoining Air Force training bases, EPA regulators, the firefighting community in general, and all manufacturers and users of halon extinguishing agents.

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GLOSSARY

Ceiling Limit	The concentration that should not be exceeded during any part of the working exposure (Threshold Limit Value—Ceiling).
CEM	Continuous emission monitor. Any instrument capable of providing an essentially continuous and real-time output proportional to the concentration of a compound of interest.
FTIR	Fourier transform infrared. An interferometer-based spectroscopic technique that can simultaneously identify and quantify mixtures of volatile organic and inorganic compounds.
GC/MS	Gas chromatography/mass spectrometry. An analytical technique that first separates a sample by boiling point in a gas chromatograph and then analyzes the distinctive mass fragment pattern produced by passing the separated sample through a strong ionization source.
HC	Hydrocarbon. Any flammable compound of carbon and hydrogen, such as methane, propane, or hexane. Also, a mixture of such compounds, such as gasoline, JP-4, or kerosene.
IDLH	Immediately dangerous to life or health. Defined as the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without experiencing any escape-impairing or irreversible health effects.
LC ₅₀	Lethal concentration, 50 percent. Usually a rodent-based inhalation assay indicating the concentration necessary to produce 50 percent mortality in an exposed population.
MDL	Method detection limit. The GC/MS detection limit for a compound, usually defined as three times the detector noise.
MEI	Maximum exposed individual. The hypothetical individual who remains at the highest concentration point of a plume at a prescribed distance from a source.
PEL	Permissible exposure limit. Maximum safe occupational exposure established by the Occupational Safety and Health Administration, usually based upon an 8-hour time-weighted average.

PUF	Sampling system used for semivolatile organic compounds, (EPA Ambient Method TO-4) based on the use of a polyurethane foam cartridge with a glass fiber particulate filter.
RIC	Reconstructed ion chromatogram. A GC/MS output showing the total ion current from the detector plotted against elution time.
STEL	Short-term exposure limit. The concentrations to which workers can be continuously exposed for short periods of time without suffering adverse effects. It is a 15-minute time-weighted average exposure that should not be exceeded at any time during a work day.
SVO	Semivolatile organic. Organic compounds with boiling points above 100°C. May not be in the vapor state as sampled. Sampling methods must include provisions for collection of mist droplets or material bound to solid particles.
Target Compounds	Selected list of compounds of importance to the study and/or realistic possibility for their presence. Initial target compound list was provided by the Air Force and was modified by MRI after concluding the Screening Study.
TIC	Tentatively identified compound. Compound identifications based on a GC/MS library search without confirmation by recent analysis of a known sample prepared from the pure compound.
TLV	Threshold Limit Value. Inhalation (ceiling) limit established by the American Conference of Government Industrial Hygienists.
TWA	Time-Weighted Average. Refers to concentrations of airborne toxic materials which have been weighted for a certain time duration, usually 8 hours.
VOC	Volatile organic compound. Organic compounds having boiling points below 100°C. Normally present in the vapor state in ambient air samples. Gaseous sampling techniques are usually appropriate.

SECTION I

INTRODUCTION

A. OBJECTIVES

The U.S. Air Force Halon Replacement Program is concerned about the exposure of personnel to chemical compounds during fire-training exercises as well as during actual flightline fires. The Air Force also is interested in understanding the environmental fate and effects of chemical compounds resulting from the combustion of halocarbon firefighting agents and jet fuel during these training exercises or fires. The purpose of this study was to assess the hazards associated with the inhalation of these compounds and to evaluate the fate and effects of the halocarbon/jet fuel combustion products.

B. BACKGROUND

Fire-training exercises are conducted routinely for Air Force personnel at several locations throughout the United States. In a typical training exercise, a controlled fire is ignited and firefighter personnel are directed to extinguish the blaze, using safe and effective techniques. Jet fuel (JP-4) is typically combusted in a circular test pit or cement dike to create the exercise scenario. During these exercises, firefighters can be exposed to the airborne vapors, aerosols, and gases from both the jet fuel and the extinguishing agent, and the combustion products of each. An additional concern is that these chemicals and combustion products are emitted to the atmosphere. Once in the atmosphere, long-range transport, chemical transformation, and dry deposition can occur, resulting in the possibility of additional human exposure and adverse environmental effects.

C. SCOPE/APPROACH

This report describes a detailed state-of-the-art air-monitoring survey of representative training exercise test burns to assess the hazards of burning fuel only and the use of the existing extinguishing agent as compared to proposed replacement agents. Techniques of atmospheric transport modeling were employed to project the fate and effects of plume components leaving the training site. The main field exercise was conducted from October 15 through October 18, 1991.

The specific objectives of this study were as follows:

- Determine the species of airborne chemical compounds emitted from a test burn of JP-4 jet fuel in a 75-square foot flowing fire test pit (10 feet in diameter).

- Determine the species of airborne compounds emitted during firefighting training exercises when Halon 1211 was used to extinguish a JP-4 fire in a 75-square foot flowing fire test pit.
- Determine the species of airborne compounds emitted during the firefighting exercises when the proposed replacement agents (perfluorohexane and HCFC-123) were used to extinguish a 75-square foot flowing JP-4 fire.
- Assess the level of exposure based on the firefighter's position relative to the fire.
- Assess health hazards to the firefighter associated with using the replacement extinguishing agent relative to the health hazards associated with using Halon 1211 and the fire-only baseline tests.
- Recommend steps to reduce firefighter exposure to toxic air contaminants.
- Evaluate the fate and effects of combustion products to the atmosphere during training exercises, including:
 - The potential for chemical transformation and long-range atmospheric transport.
 - The potential for human exposure (via ingestion and dermal contact) and adverse environmental effects resulting from dry deposition onto soils, crops, surface waters, and dermal surfaces, and any subsequent groundwater contamination.

MRI conducted a Screening Study, as a precursor to the Main Test, at the New Mexico Engineering Research Institute (NMERI) test site in Albuquerque during the period July 29 through August 1, 1991. The site elevation was 5,300 feet above sea level. Tests were performed with fuel only and with the current agent, Halon 1211. The primary objectives of the Screening Study were to develop and evaluate sampling procedures and sampling matrices and to identify significant pyrolysis products generated during training exercises. Results of the Screening Study were used to design the revised sampling, analysis, and modeling plan for the Main Test.

In the Main Test (as in the Screening Study), NMERI set up the test burns, ignited the fires, and provided the firefighter and extinguishing agent to put out the fires. Field sampling and analysis of the samples were also performed by MRI.

The remainder of this report is divided into seven sections and three appendices. Section II presents a brief summary of the preliminary Screening Study. Section III presents the results of the Main Test. Section IV discusses firefighter exposure, and

Section V discusses community exposure. Section VI discusses the quality assurance checks performed on the data. Section VII lists the primary conclusions, and Section VIII presents the recommendations.

Appendix A contains the detailed results from the Screening Study, Appendix B contains sample calculations, and Appendix C contains further data from the Main Test.

SECTION II

SCREENING STUDY

A preliminary Screening Study test was conducted at the New Mexico Engineering Research Institute (NMERI) test site from July 29 through August 1, 1991. Test site elevation was 5,300 feet above sea level. The purpose of the Screening Study was to:

- Evaluate the effectiveness of sampling and analytical protocols and procedures.
- Assess any analytical interference problems.
- Ensure that all equipment was performing appropriately.
- Attempt to qualitatively identify compounds present in the plume and at the firefighter position. Semiquantitative air concentrations were to be reported for all detectable compounds.

A. TEST DESIGN

All tests were conducted with a 75-square foot pool fire of JP-4. Only the baseline agent, Halon 1211, was evaluated. The emissions that occur during a simple test with the baseline agent had to be determined before comparing different agents. In the Screening Study, stationary area samples were collected at two locations: immediately adjacent to the firefighter and within the plume itself. Table 1 presents the preliminary list of target compounds together with the intended sampling and analysis methods. Where multiple methods are listed, the compound may be detected by all the methods, depending on concentration.

Integrated air samples of volatile organic compounds (VOCs) were collected in passivated Summa[®] canisters and on Tenax[®]/carbon molecular sieve (CMS) adsorbent tubes (also referred to as Tenax[®]/Carbosieve[®]). These samples were shipped to MRI for analysis by gas chromatography/mass spectrometry (GC/MS). Integrated air samples of semivolatile organic compounds (SVOs) were collected by EPA Ambient Method TO-4 using a polyurethane foam cartridge with a glass fiber filter (PUF). Subsequent analyses of the PUF samples were by GC/MS. Particulate samples were collected on preweighed filters for determination of total mass by gravimetric analysis and for organic compounds by GC/MS analysis. Acid gases and other volatiles were monitored by Fourier transform infrared spectroscopy (FTIR) on the downwind edge of the plume.

TABLE 1. LIST OF TARGET COMPOUNDS AND SAMPLING METHODS.*

Category	Compound	Method
Fire extinguishing agents	Halon 1211	a,c,e
Fuel	JP-4	a,c,d,e
Acutely toxic gases	Phosgene (COCl ₂)	a
	Hydrogen chloride (HCl)	a
	Hydrogen fluoride (HF)	a
	Hydrogen bromide (HBr)	a
	Carbon monoxide (CO)	a,b
	Hydrogen cyanide (HCN)	a
	Perfluoroisobutene (PFIB)	a,c,e
Carcinogens/teratogens	Polynuclear aromatic hydrocarbons (PAHs)	d
	Benzene	c,e
	Dioxins/furans	a,d
	Ethylene dibromide (EDB)	d
	Ethylene dichloride (ECB)	a,c,e
	1,3-Butadiene	a,c,e
	Carbon tetrachloride	a,c,e
	Trichloroethylene (TCE)	a,c,e
	Perchloroethylene (PCE)	a,c,e
Other contaminants	Phenols	d
	Toluene	a,c,e
	Xylene	a,c,e
	Nitrogen oxides (NO _x)	a
	Sulfur oxides (SO _x)	a
	1,1,1-Trichloroethane (TCA)	a,c,e
	Particulates	d

^a FTIR^b CO monitor^c Summa[®] canister^d PUF^e Tenax[®]/Carbosieve[®]

* Other target compounds may be added or substituted after initial analyses.

The actual Screening Study consisted of six test runs of varying conditions outlined in Table 2. Runs 1 and 2 consisted of burning jet fuel (only) for a brief period (about 5 minutes) to allow collection of background FTIR data and familiarization with sampling techniques in the firefighting environment. Run 3 consisted of burning jet fuel (only) with the full array of sampling techniques. This run was aborted because an excessive amount of JP-4 fuel was burned, which resulted in a long sampling time.

TABLE 2. FINAL SCREENING STUDY TEST MATRIX.

Run No.	Test type	Sampling methods	Fire out	Sample locations	Notes
1	Fuel only	FTIR	Yes	Plume	-
2	Fuel only	FTIR	Yes	Plume	-
3	Fuel only	ALL	Yes	Plume, FF	Aborted due to length of burn
4	Fuel + H-1211	FTIR, vertical profile	Yes	Plume, FF	-
5	Fuel + H-1211	ALL	Yes	Plume, FF	-
6	Fuel only	ALL	Yes	Plume, FF	Temp. profile

ALL = PUF
 Tenax®/Carbosieve®
 Summa®
 FTIR
 CO monitor
 FF = Firefighter location

Runs 4 and 5 consisted of burning jet fuel, then extinguishing the fire with Halon 1211. Although the fire could be extinguished in several seconds, the fire was "nursed" along for about 2 minutes, neither letting it burn uncontrolled nor allowing it to be completely extinguished by agent. This allowed enough time for meaningful samples to be collected. Sampling continued after the fire was extinguished for approximately 5 minutes to collect emissions from smoke and offgases. During Run 4, Summa® canisters were used to collect samples at ankle, waist, and breathing height. Samples collected at these three positions are hereafter referred to as the "vertical profile." Run 5 used all of the sampling techniques and the same test conditions described in Run 4. Run 6 included all sampling techniques used on the fuel-only fire.

A temperature profile of the plume was attempted using the FTIR as an optical pyrometer. During this test, the FTIR scanned a vertical and horizontal traverse across the flame zone to form a "cross." The intention was to interpret the FTIR data using Planck's blackbody curve to allow temperatures to be determined. However, the profile was of limited value due to rapid changes in plume position and intensity.

Firefighter (FF) samples were collected directly adjacent to where the firefighter stood while he extinguished the fire (Figure 1). Samples were taken at breathing height, except for the "vertical profile" method of Run 4.

In addition to the samples listed previously, one background sample (upwind) was collected for each of the sampling methods (Summa®, PUF, and Tenax®/Carbosieve®). Blank samples, which consisted of sample collection media, were also collected in the field. They were handled in the same manner as the regular samples, except no sample air was pulled through them. Blanks and upwind samples ultimately showed traces of benzene, toluene, and other compounds associated with the fuel.

Plume samples (except for FTIR) were collected using a plume-sampling probe and manifold. Essentially the sampling probe was placed directly in the plume, and sample gas was drawn into the manifold. The manifold then split the sample among the Summa®, PUF, Tenax®/Carbosieve®, and CO monitors, which were all kept at ground level. A 25-foot Teflon®-lined sample probe was used.

B. RESULTS

During the Screening Study, only JP-4 and Halon 1211 were evaluated. The summary results (shown in Table 3) of the Screening Study are:

- Potential firefighter exposure to hydrogen fluoride (HF), hydrogen bromide (HBr), and hydrogen chloride (HCl) in the downwind plume was above the respective Permissible Exposure Limits (PELs) during agent addition, and peak concentrations were above the Immediately Dangerous to Life or Health (IDLH) limits. This potential exposure to the firefighter could occur if the plume shifted position and engulfed the firefighter.
- Firefighter exposure to Halon 1211 depends on height, increasing one-hundredfold from head to ankle height.
- The plume sampling probe must be movable during the test period.
- Many other compounds were found at trace levels, but none approached toxic levels.

Screening Study results are presented in greater detail in Appendix A.

In addition to the above main points, the Summa® and Tenax®/Carbosieve® samples showed consistently similar results, primarily finding Halon 1211 and fuel components. The CO monitors failed to show any measurable concentrations. The PUF samples showed traces of various polynuclear aromatic hydrocarbons. The carbon molecular sieve trap showed inconsistent results during analysis. The FTIR detected Halon 1211, HCl, HBr, HF, JP-4, CO, acetylene, and an unknown compound at rapidly changing concentrations. HCl, HBr, and HF were all present at hazardous

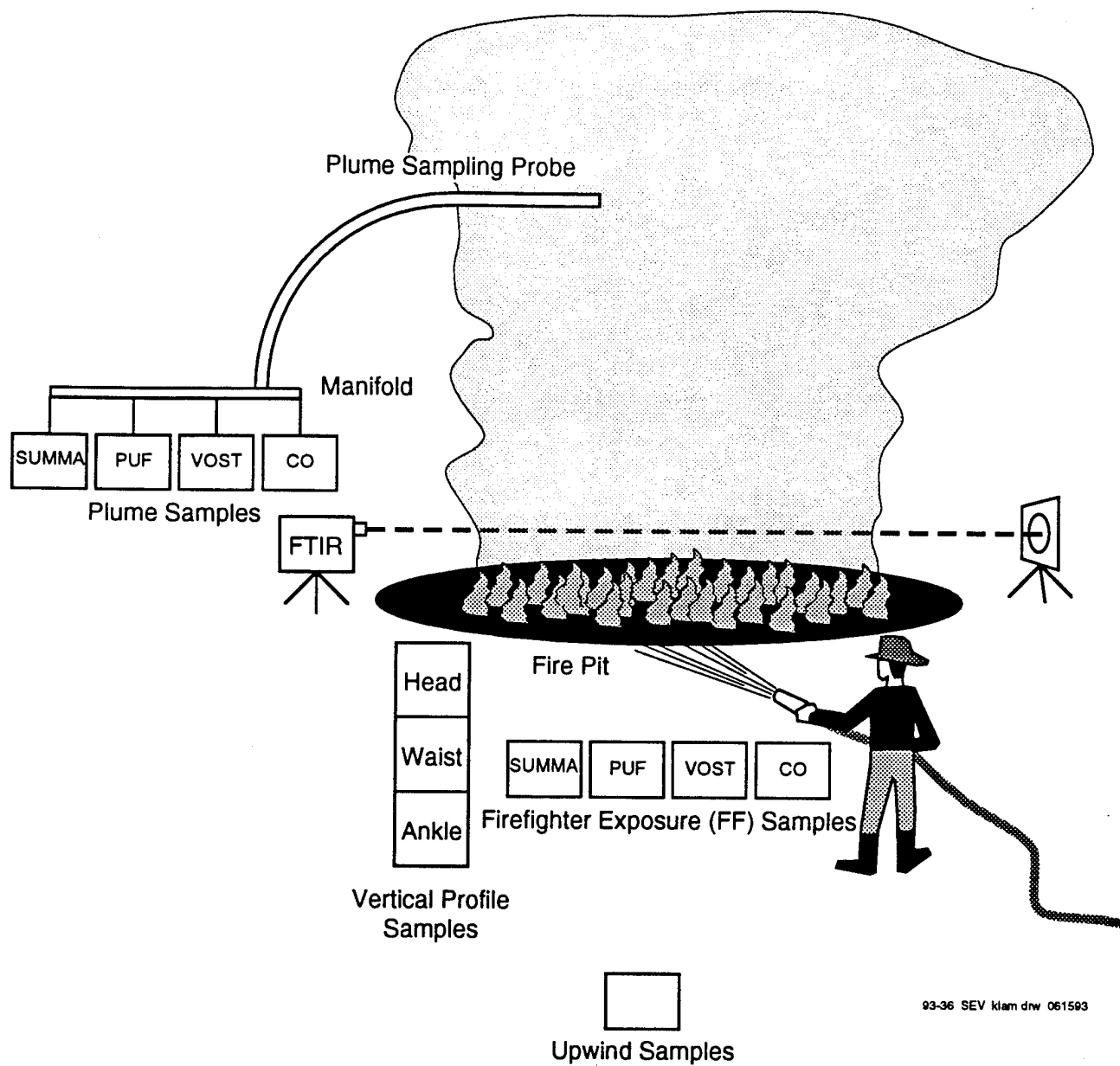


Figure 1. Schematic of Screening Study Sampler Array.

TABLE 3. SCREENING STUDY SUMMARY RESULTS (units are ppm, v/v).

Method	Compound	JP-4 only		Halon 1211	
		FF	Plume	FF	Plume
Summa [®] and Tenax [®] /Carbosieve ^a	Halon 1211	-	0.009-0.03	5.6-34	0.4-25
Summa [®] and Tenax [®] /Carbosieve ^a	1,3-Butadiene	-	0.014-0.1	-	0.012
Summa [®] and Tenax [®] /Carbosieve ^a	Benzene	0.01-0.04	1.9-4.7	0.042-0.047	0.4-0.6
Summa [®] and Tenax [®] /Carbosieve ^a	Toluene	0.02-0.06	0.17-0.33	0.07	0.14-0.16
Summa [®] and Tenax [®] /Carbosieve ^a	p-Xylene	0.01	0.03	0.035	0.044
Summa [®] and Tenax [®] /Carbosieve ^a	JP-4	0.17	0.97	2.5	3.1
FTIR ^b	Acetylene	-	1.2	-	2.5
FTIR ^b	Halon 1211	-	-	-	520-840
FTIR ^b	HCl	-	-	-	40
FTIR ^b	HBr	-	-	-	44-51
FTIR ^b	HF	-	-	-	15-18
FTIR ^b	COF ₂	-	-	-	9-15
FTIR ^b	JP-4	-	37	-	33-51
FTIR ^b	CO	-	57	-	86-132
PUF ^a	Acenaphthylene	-	-	-	0.018
PUF ^a	Fluoranthene	-	-	-	0.004
PUF ^a	Phenanthrene	-	-	-	0.004
PUF ^a	Pyrene	-	-	-	0.003

^a Average concentration for entire test period.

^b Average during the fire only (JP-4 only) or agent application (Halon 1211) phase.

levels in the near-plume area. One problem was with the operation of the plume-sampling probe, which proved difficult to position in the plume, because no adjustments were possible once the fire had been ignited.

Carbonyl fluoride was identified as the unknown compound only after the Screening Study was completed. It was not yet identified, nor was its concentration known (and therefore not discussed), until the Main Test section of this report.

C. SUMMARY

The Screening Study objectives were met, allowing results of the Screening Study to be used in design of the Main Test matrix. The Screening Study found that for the baseline agent (Halon 1211) that was tested, HF, HBr, and HCl concentrations in the downwind plume were all above their respective PELs and occasionally peaked above their IDLH limits as well. Other volatile and semivolatile compounds were found at trace levels, but none approached toxic levels. The selected test methods of FTIR and PUF were very effective in collecting the intended samples. The Summa[®] canisters and Tenax[®]/Carbosieve[®] traps showed consistently similar VOC results, as expected for these two methods. The CO monitors failed to show any measurable concentrations and were dropped from use in the Main Test.

SECTION III

MAIN TEST

The sampling and analytical methods used for the Air Force Main Test were based on the Screening Study results and recommendations presented at a subsequent project meeting at MRI (17 September 1991). Objectives for the Main Test included the identification and quantitation of both organic and inorganic species released during firefighting exercises. The sampling and analytical methods employed were chosen to best characterize the volatile organic compounds (VOCs), semivolatile organic (SVOs) compounds, and polychlorinated dioxins and furans (PCDD/PCDFs), utilizing EPA analytical procedures. In addition to the EPA procedures, volatile toxic gases and acid gases were identified and quantified using procedures developed by MRI for these tests.

At the 17 September meeting, it was determined that for the VOCs, Carbosieve® adsorbent cartridges provided redundant information and should be eliminated for the Main Test. In addition, it was recommended that the Tenax® cartridges be replaced with a combination Tenax®/charcoal cartridge to better facilitate the collection of highly volatile compounds. FTIR was also used to monitor some VOCs. The additional requirement for PCDD/PCDF analysis was accomplished by splitting the PUF cartridge sample extract for subsequent GC/MS analysis via different test methods.

The Screening Study showed that significant concentrations of acid gases were detected by the FTIR. This measurement increased the importance of FTIR from an experimental technique to the most critical measurement. Because of this importance, a second acid gas detection method was needed to provide additional information during the Main Test. Acid gas impinger trains were considered. However, a cheaper and simpler alternative was to use a large number of length-of-stain acid indicator tubes that could quickly measure acid gases at several positions within the test area. This simpler alternative was chosen as the method used to provide additional information.

It was decided to operate the FTIR in the same way as in the Screening Study. The FTIR had been placed in about the best position for the beam, located on the downwind edge of the fire pit at breathing height. The Draeger length-of-stain tubes were added to confirm and provide location and width-of-plume information for the acid gases. The FTIR also provided good CO concentrations, so that the CO continuous emission monitor (CEM) analyzers were not needed for the Main Test.

Because of the changes to the Main Test as described above, a more extensive QA Plan was necessary. The revised QA Plan included a more comprehensive list of expected target analytes, with replicate analyses and full accuracy and precision measurements. However, since the testing of new extinguishing agents was involved

(perfluorohexane and HCFC 123), a comprehensive list of target analytes prior to analyses was not possible.

A. TEST DESIGN

The test matrix was set up as follows:

- One test burn of a fuel fire without using a firefighting agent
- One test burn with agent Halon 1211
- Two test burns with agent HCFC 123
- Two test burns with agent perfluorohexane (PFH)

The intended analysis methods to be used during all six test burns are indicated in Table 4.

The design called for extractive samples to be collected from: (1) an upwind location, (2) the firefighting area (breathing zone), (3) a downwind location, and (4) the plume. In addition, FTIR was to be used to scan the plume to determine air concentrations of organic compounds, vapors, and inorganic gases. Table 5 shows the targeted compounds.

Upwind samples were collected one time only for Summa®, Tenax®/charcoal, and PUF collection methods. As such, upwind samples are only discussed in the VOC and SVOC segments of the Test Results subsection. Clean air background FTIR scans, however, were recorded immediately before each test. At least one length-of-stain tube was always at an upwind location for each test.

This sampling scheme provided approximately 80 extractive samples (exclusive of QA samples) requiring organic analysis by methods such as GC or GC/MS. Including analyses required for QA purposes, approximately 100 sophisticated analyses were to be performed.

1. Facilities

The test facilities were located on Kirtland Air Force Base, Albuquerque, New Mexico, at the Civil Engineering Research Facility (CERF). The site elevation was 5,300 feet above sea level. The tests were conducted within a wind fence enclosure (Figure 2). This enclosure was constructed of Tenax® Reparella monooriented netting positioned as a pair of concentric circles totally surrounding the test area to minimize wind effects. The outer fence diameter was 140 feet; the inner fence diameter was 85 feet; and the height of each fence was 18 feet. A circular fire pit was located in the center of this enclosure.

TABLE 4. SAMPLING AND ANALYSIS METHODS
FOR FIREFIGHTER STUDY.

Analyte(s)	Sampling method	Analysis method
Volatile organic compounds	Tenax®/charcoal adsorption	GC/MS (Modified EPA Method T02 and 8260)
	Summa® passivated canister	GC/MS (Modified EPA Method T014 and 8260)
Semivolatile organics compounds	Polyurethane foam (PUF) absorption	GC/MS (Modified EPA Method T04 and 8270)
Polychlorinated dioxins and furans	PUF	MRI Modified EPA Method GC/MS 8290
Total particulate mass and bound organic carbon	Filtration	Gravimetric and GC/MS
Volatile toxic gases	Continuous monitor	Portable Fourier transform infrared analyzer
	Draeger tube w/personnel sampler pump	Length-of-stain tube
Fire extinguishing agents	Canister, vertical profile	Gas chromatography/flame ionization and electron capture detectors

TABLE 5. MAIN TEST LIST OF TARGET COMPOUNDS
AND SAMPLING METHODS.

Category	Compound	Method
Fire extinguishing agents	Halon-1211	a,c,e
	HCFC 123	a,c,e
	Perfluorohexane (PFH)	a,c,e
Fuel	JP-4	a,c,d,e
Acute toxic	Hydrogen chloride (HCl)	a,b
	Hydrogen fluoride (HF)	a,b
	Hydrogen bromide (HBr)	a,b
	Carbon monoxide (CO)	a
	Carbonyl fluoride (COF ₂)	a,b
Carcinogens/teratogens	Polynuclear aromatic hydrocarbons (PAHs)	d
	Benzene	a,c,e
	Dioxins/furans	d
	Benzo[a]pyrene (BaP)	d
	Ethylene dibromide (EDB)	a,c,e
	Ethylene dichloride (ECB)	a,c,e
	1,3-Butadiene	a,c,e
	Carbon tetrachloride	a,c,e
	Trichloroethylene (TCE)	a,c,e
	Perchloroethylene (PCE)	a,c,e
Other contaminants	Phenols	d
	Toluene	a,c,e
	Xylenes	a,c,e
	Nitrogen oxides (NO _x)	a
	Sulfur oxides (SO _x)	a
	1,1,1-Trichloroethane (TCA)	a,c,e

a = FTIR

b = Draeger tube

c = Summa® canister

d = PUF

e = Tenax®/charcoal

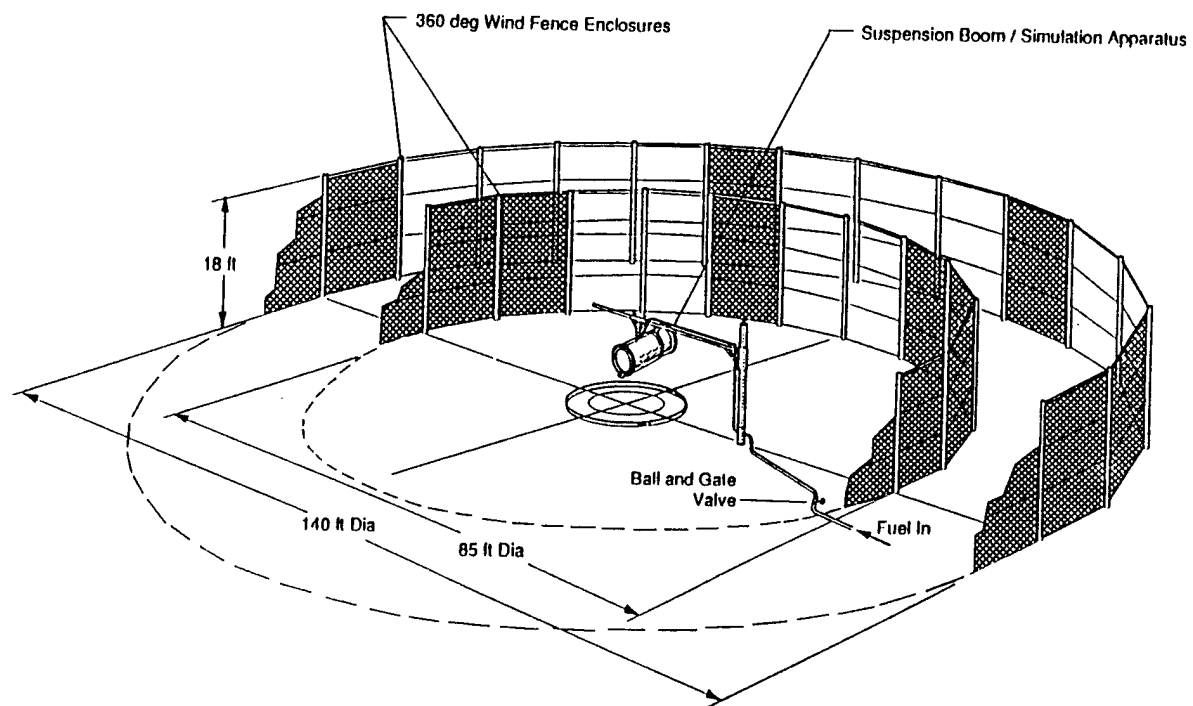


Figure 2. Wind fence enclosed test site.

2. Materials and Apparatus

Unlike the Screening Study, for which fires were simply ignited in the circular fire pit, the Main Test setup was designed to simulate an aircraft engine fire. The scenario prescribed an engine attached to the bottom surface of an aircraft wing with a fuel line that has broken, spilling fuel from the engine onto the runway. The simulation apparatus was constructed of two different-sized barrels welded one inside the other (Figure 3). The inner barrel was a standard 55-gallon drum. The outer barrel was an overpack drum with about a 6-inch larger radius than the inner drum. The smaller barrel was welded inside the larger barrel with support rods to keep the inner barrel centered. This structure was suspended over the fire pit with the front edge 15 degrees lower than the rear of the apparatus on a swivel mount attached to a horizontal steel pipe boom. A fuel spray system was built into this apparatus to provide a constant supply of running fuel to the drums. Fuel flowed through the inner barrel, onto the outer barrel and out of the whole apparatus into the circular fire pit 4 feet below.

The fuel used for this testing was Military Grade JP-4. This naphtha-based fuel contains several additives, including a fuel system icing inhibitor, a corrosion inhibitor, and a conductivity additive. Previous testing conducted at New Mexico Engineering Research Institute (NMERI) and other independent sources has shown that the expected particulate loading from the emissions of a JP-4 training fire at a constant burn rate and standard conditions is 190 to 210 milligrams per standard cubic meter (mg/scm) for every 45 kilograms of fuel burned.

The extinguishers used in this testing were standard Amerex Model 600 150-pound wheeled flightline units. These units were filled with either 150 pounds of Halon 1211, or 120 pounds of HCFC 123 or perfluorohexane. The extinguishers were pressurized to 200 psig for Halon 1211 and to 230 psig for the other agents.

Two types of nozzles connected to the hoses were used. The standard flightline smooth-bore nozzle normally used with the Amerex Model 600 unit was used for the Halon 1211 tests. An adjustable spray nozzle was used in one of the Halon 1211 tests and in all the HCFC 123 and perfluorohexane test. The adjustable nozzle can be set in multiple spray pattern positions and can easily be adjusted during a test. This nozzle was normally set in a predetermined position that delivered the HCFC 123 and perfluorohexane to the fire in an effective extinguishing spray pattern. The optimum spray setting was slightly different for HCFC 123 than the perfluorohexane agent.

Video cameras were positioned at various points around the test array to record the fire characteristics, as well as to allow accurate timing of the various fire phases to be measured. The videotapes are part of the project archives.

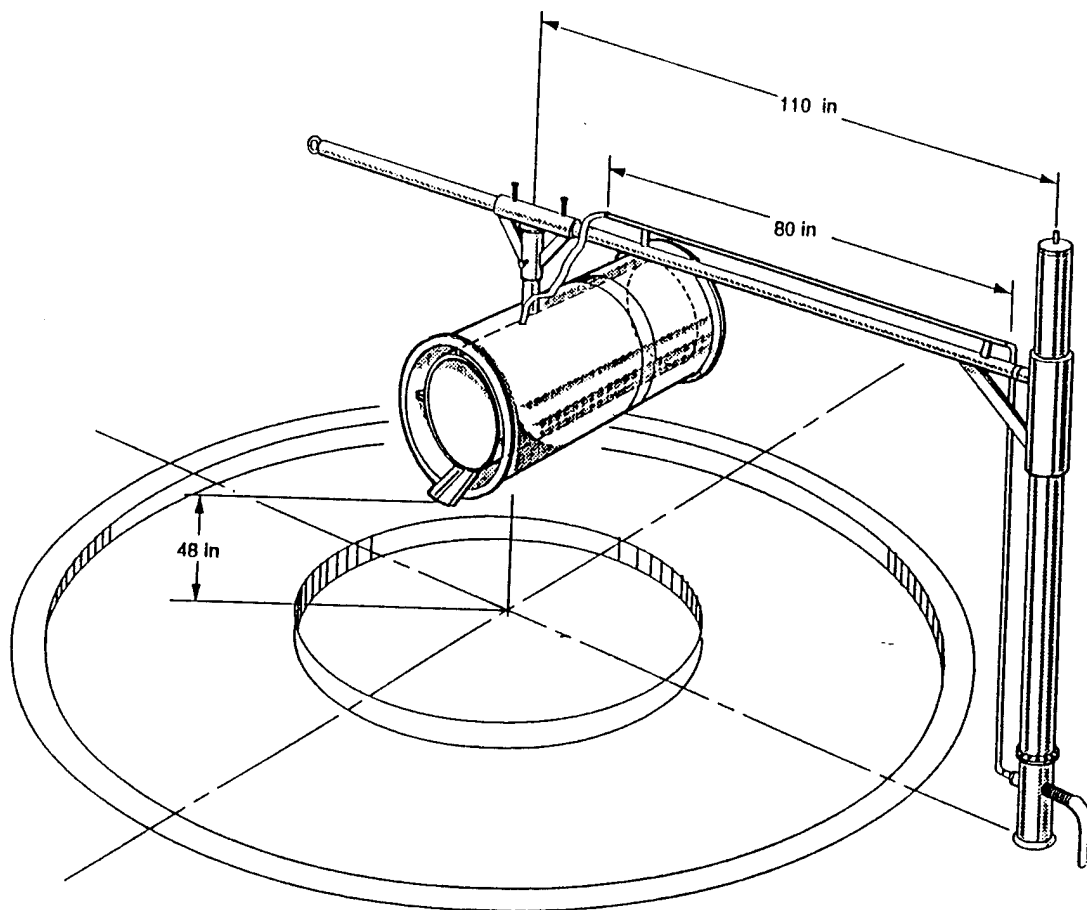


Figure 3. Three-dimensional running fuel apparatus.

B. RESULTS

Target compounds listed on Table 5 will not be discussed in the text of this report if they were not observed to be present in the analysis results.

1. Test Conditions

Due to field observations and equipment problems, the original test matrix was modified slightly during the test series. Three additional test runs (one for each agent) were added to the scope, using only the FTIR and Draeger tubes for those runs. The intention was to gain more complete data on the acid gas characteristics and plume behavior. One FTIR run was repeated due to equipment problems with the instrument immediately prior to the beginning of Run 6. Table 6 shows the final Main Test matrix of test runs as they were performed in the field. Note that the fire was not extinguished in all cases. Also, note that upwind sampling was only necessary for PUF, Summa®, and Tenax®/charcoal sample collection and was performed as a separate run.

Runs 1, 2, 4, 5, 6, and 7 followed the original test plan, collecting the full array of samples at the plume, firefighter, and downwind locations (Figures 4a and 4b). An FTIR malfunction occurred during Run 6, so the FTIR and Draeger tube portions of that test were repeated as Run 8. The FTIR was placed in a regular-angle path for direct plume sampling during Runs 1, 2, 4, 5, 7, and 8. Runs 3, 9, and 10 consisted of FTIR and Draeger tube testing only. Additionally, the FTIR was placed in a long-angle path to sample a wider section of the plume during those three tests.

Table 7 summarizes the test conditions and parameters from the Main Test in October 1991. Note that the fire was not fully extinguished during all the tests, which increased the amount of fuel consumed during those runs in comparison to the runs in which the fire was successfully put out.

The following discussion summarizes each test run conducted during the Main Test study. Figure 5a shows sampling locations for Runs 1 and 2. Figure 5b shows sampling locations for Runs 4 through 7. Figure 6a shows sampling locations for Run 8, and Figure 6b shows sampling locations for Runs 9 and 10.

Run 1: The first run was conducted to test the emissions from a 75-square foot fuel fire without using a firefighting agent. The standard method of flowing 2 gallons of fuel through the upper apparatus and allowing it to accumulate in the lower containment ring was followed. The fuel was then ignited, the fire was allowed to burn for 3 minutes, and the fuel flow was turned off, allowing the fire to burn to completion. A total of 20 gallons of fuel were consumed in this test. All methods of emission sampling were used for this run.

TABLE 6. FINAL MAIN TEST MATRIX.

Run No.	Test type	Sampling methods	Fire out	Sample locations*	Notes
1	Fuel only (baseline)	All	N/A	Plume, FF, downwind	-
2	H-1211	All	No	Plume, FF, downwind	-
3	H-1211	FTIR, D.T.	Yes	Downwind	FTIR long-angle
4	HCFC 123	All	No	Plume, FF, downwind	-
5	HCFC 123	All	Yes	Plume, FF, downwind	-
6	Perfluorohexane	All but FTIR	No	Plume, FF, downwind	No FTIR data
7	Perfluorohexane	All	Yes	Plume, FF, downwind	-
8	Perfluorohexane	FTIR, D.T.	Yes	Plume, downwind	Repeat of Run 6, FTIR only
9	Perfluorohexane	FTIR, D.T.	Yes	Downwind	FTIR long-angle
10	HCFC 123	FTIR, D.T.	Yes	Downwind	FTIR long-angle

ALL = PUF
 Tenax®/charcoal
 Summa®
 Vertical canisters
 FTIR
 Draeger tubes (D.T.)

FF = Firefighter location

* Upwind PUF, Summa®, Tenax®/charcoal samples were collected as a separate run. No separate upwind sampling was required for FTIR or Draeger tube collection. The regular location of the FTIR beam was in the plume, the long angle FTIR line of sight was near the downwind samplers.

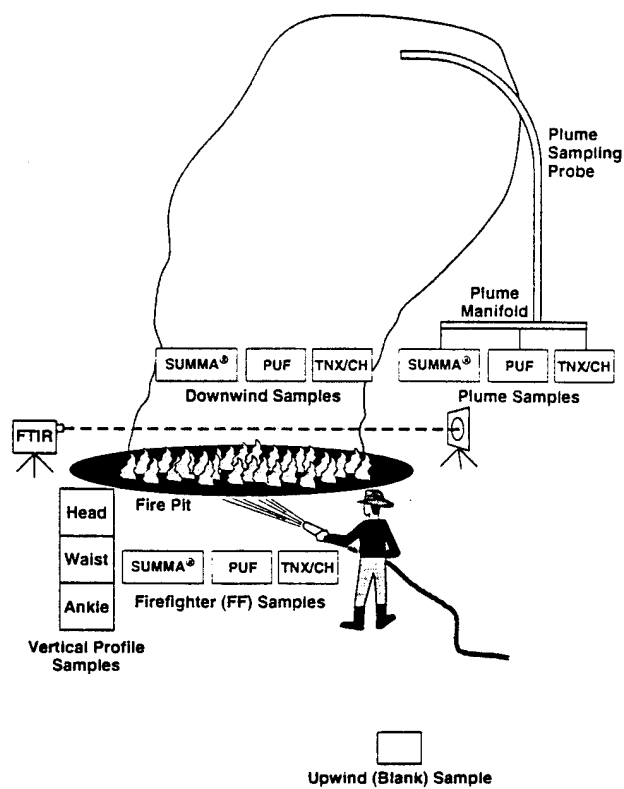


Figure 4a. Horizontal view of sampler array.

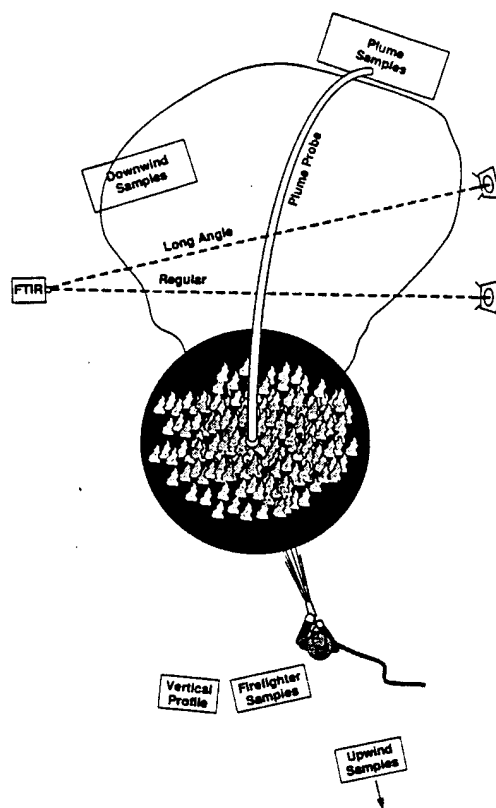


Figure 4b. Vertical view of sampler array.

TABLE 7. MAIN TEST CONDITIONS SUMMARY

	Run No.									
	1	2	3	4	5	6	7	8	9	10
Date	15 Oct 91	15 Oct 91	15 Oct 91	16 Oct 91	17 Oct 91	17 Oct 91	18 Oct 91	18 Oct 91	18 Oct 91	18 Oct 91
Time of day	10:20 a.m.	12:30 p.m.	1 p.m.	9:10 a.m.	8:40 a.m.	11:30 a.m.	8:30 a.m.	11:15 a.m.	11:45 a.m.	12:05 p.m.
Ambient temp (°F)	70	80	82	70	68	75	65	78	79	80
Wind direction, speed (mph)	Calm	SSW, Gusts 1 to 5	SSW, 1 to 5	Calm	Calm	SSE, 1 to 2	Calm	Calm	Calm	Calm
Fuel amount (gal)	20	8.6	7.3	14	4.4	5.9	4.8	3.4	4.3	4.0
Fuel flow rate (gpm)	4.5	3.6	4.1	6.5	4.2	4.2	3.7	3.3	3.2	3.0
Agent type	None	H1211	H1211	HCFC123	HCFC123	PFH	PFH	PFH	PFH	HCFC123
Agent amount (lb)	N/A	150	65	130	99	124	67	88	100	88
Agent flow rate (lb/s)	N/A	3.2	2.0	2.5	4.7	3.2	4.9	5.1	4.5	4.6
Nozzle type	N/A	ADJ	STD	ADJ	ADJ	ADJ	ADJ	ADJ	ADJ	ADJ
Extinguisher pressure (lb/in. ²)	N/A	200	200	200	230	230	230	230	230	230
Preburn duration (s)	N/A	40	38	28	13	12	13	14	16	14
Fire duration (min)	4:30	2:00	1:17	3:46	0:35	2:28	0:27	0:31	0:39	0:33
Types of samples	All	All	FTIR, D.T.	All	All	All	All	FTIR, D.T.	FTIR, D.T.	FTIR, D.T.
Fire extinguished	N/A	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes

D.T. = Draeger tube sampling.

STD = Standard.

ADJ = Adjustable.

All = PUF

Tenax®/charcoal

Summa®

Vertical canisters

FTIR

Draeger tubes (D.T.)

The diagram illustrates the layout of a test facility. It features two concentric circles: an inner circle labeled "inner Wind Screen" and an outer circle labeled "Outer Wind Screen". At the center is a fire source, represented by a circle with flames. A person is shown standing near the center. Various measurement points are marked with symbols: diamonds (Dräger Tube at Breathing Height), triangles (VOST), squares (PUF), and circles (SUMMA). Distances are indicated: 27.5' from the center to the inner wind screen, 37.5' from the center to the outer wind screen, 15' from the center to the VOST point, 10' from the center to the PUF point, 13' from the center to the SUMMA point, and 17' from the center to the FTIR point. A legend at the bottom left defines the symbols: diamond for Dräger Tube at Breathing Height, triangle for VOST, square for PUF, circle for SUMMA, vertical line for Vertical Profile, and square with a cross for FTIR. A north arrow points to the right, labeled "N".

LEGEND

- ◇ Dräger Tube at Breathing Height
- △ VOST
- PUF
- SUMMA®
- Vertical Profile
- FTIR

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Figure 5a. Sampler Locations—Test Runs 1 and 2.

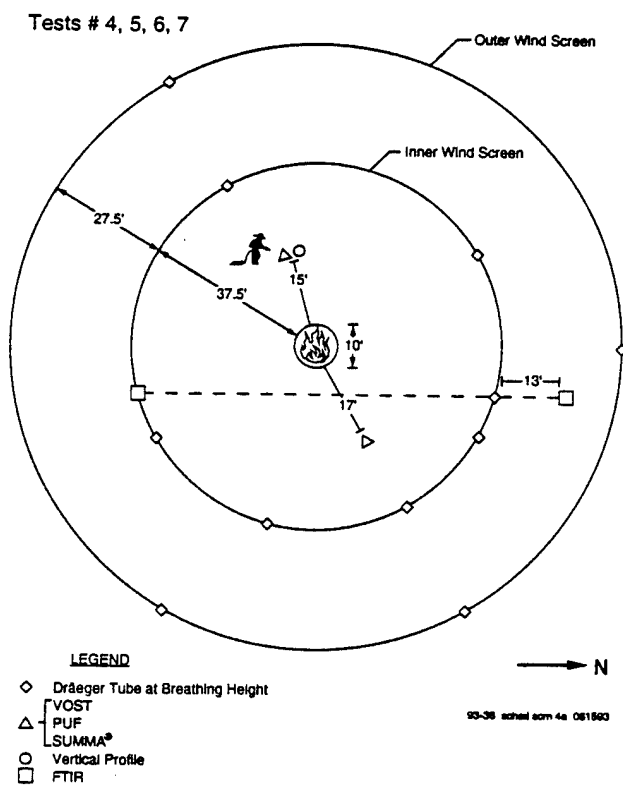


Figure 5b. Sampler Locations—Test Runs 4 through 7.

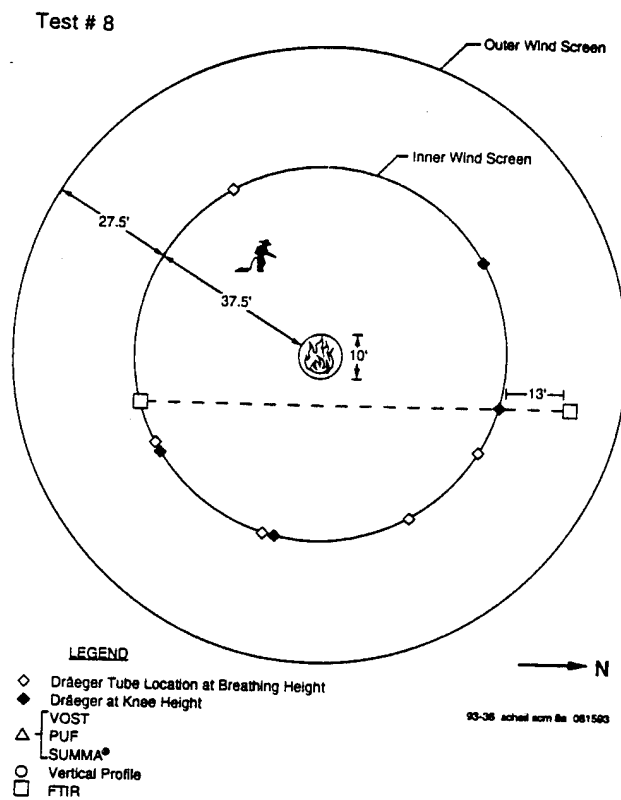


Figure 6a. Sample Locations—Test Run 8.

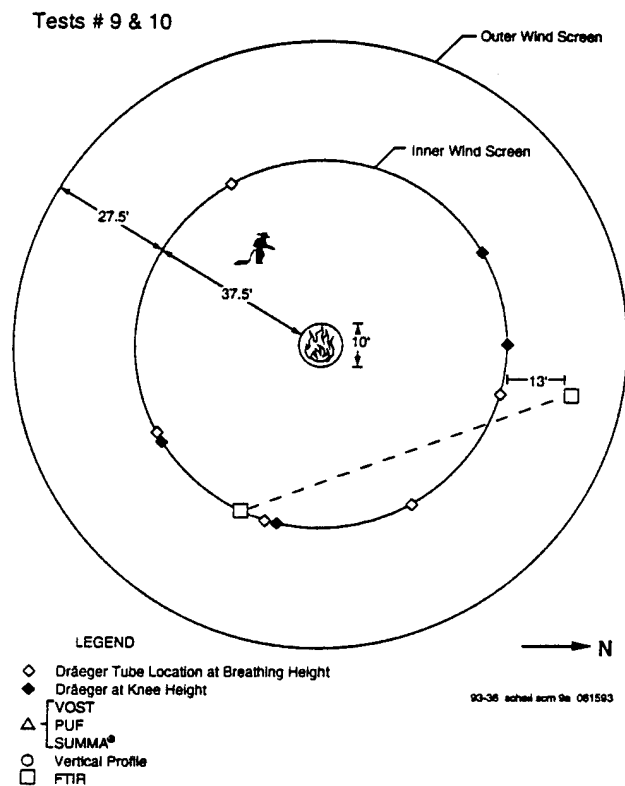


Figure 6b. Sample Locations—Test Runs 9 and 10.

Run 2: The second run was also performed during the first day of testing. The test conditions were the same as the first run except Halon 1211 was used to extinguish the fire. The preburn duration (before the extinguishing agent was applied to the fire) was extended to 40 seconds. The fire was controlled and almost extinguished several times, but was never fully extinguished.

The fire was allowed to burn to completion after the extinguisher contents were exhausted. This could be considered a "worst-case" run in which all of the extinguishing agent was ineffectively applied to the fire. The amounts of extinguishing agent and fuel used for this test were 150 pounds and 8.6 gallons, respectively. All methods of emission sampling were used for this test.

Run 3: This run was exactly like the second run, except that a standard, smooth-bore nozzle designed for Halon 1211 was used. This run was also performed during the first day of testing. The firefighter had difficulty extinguishing the fire, but did extinguish it with 65 pounds of extinguishing agent in a little over 30 seconds after a preburn duration of 38 seconds. This is twice the amount of Halon 1211 that an experienced firefighter would normally use on this type of fire. A total of 7.3 gallons of fuel was used for this run. The FTIR (long angle) and Draeger tubes were used to monitor the emissions from this run. The FTIR line of sight was moved to a longer angle to a position 5 to 10 feet further downwind of the fire.

Run 4: The fourth run was conducted on the second day of testing. The same test parameters used in Run 2 were used here, except that HCFC 123 was used as the extinguishing agent. The preburn duration lasted for about 28 seconds. The firefighter never had control of this fire, and it was never extinguished. Therefore, the fire was allowed to burn to completion. The total amounts of extinguishing agent and fuel used were 130 pounds and 14 gallons, respectively. All methods of emission sampling were used for this test.

After the fourth run, the preburn duration was shortened to approximately a 10-second period. This was done to produce a more representative test for the proposed replacement extinguishing agents.

Run 5: This was the first run on the third day of testing. The same test conditions used in Run 4 were also used for this run. The standard method of flowing 2 gallons of fuel through the upper apparatus and allowing it to accumulate in the lower containment ring was followed. The fuel was then ignited and a 10-second preburn was used. The fire was extinguished with HCFC 123; slightly more agent was used to extinguish the fire than was expected. The fire duration for this run was about 35 seconds. A total of

99 pounds of extinguishing agent was used; 75 pounds or less are normally sufficient. The amount of fuel used was 4.4 gallons. All methods of emission sampling were used for this test.

The expelled extinguishing agent formed a dense cloud that hung over the remaining fuel in the fire containment ring after completion of the fire test. This extinguishing agent cloud was present for 5 to 6 minutes after the test and inerted the fuel fumes, making it very difficult to reignite the fuel. The fuel was finally reignited and burned to completion.

Run 6: This was the second run on the third day of testing. The same test procedures followed in Run 5 were used in this run, except that perfluorohexane (PFH) was used as the extinguishing agent. The preburn duration lasted about 12 seconds. The fire was controlled somewhat by the firefighter, but was never fully extinguished. A total of 124 pounds of extinguishing agent was applied to the fire, and 5.9 gallons of fuel were consumed. All methods of emission sampling were used for this test. An FTIR malfunction caused the FTIR portion of this test to be repeated later as Run 8.

Run 7: This was the first run on the fourth and final day of testing. The test parameters were the same as in Run 6, and PFH was again used as the extinguishing agent. The fire was extinguished quickly (14 seconds) after a preburn duration of about 13 seconds, with 67 pounds of agent. A total of 4.8 gallons of fuel was used for this test, and all methods of emission sampling were utilized. The agent formed a dense cloud that inerted the fuel surface 2 to 3 minutes after the fire was extinguished.

Run 8: This run was a repeat of Run 6, and was performed on the last day of testing. The same testing parameters used in Runs 6 and 7 were used, and PFH was again the extinguishing agent. After a preburn duration of 14 seconds, the fire was extinguished after about 17 seconds. The fire was extinguished with 88 pounds of extinguishing agent. A total of 3.4 gallons of fuel was used in the run. Only FTIR sampling (in the normal position) and Draeger tube sampling of both the normal breathing height and knee height were conducted during this run. Figure 6a shows the sampler locations.

Run 9: The run was performed on the last day of testing. The same test parameters used in Runs 6 through 8 were used in this run, with PFH being the extinguishing agent. The firefighter had difficulty extinguishing this fire, and 100 pounds of extinguishing agent were used. A total of 4.3 gallons of fuel was used for this test. The FTIR line of sight was again moved to the long angle to a position 5 to 10 feet further downwind of the fire. Draeger tube sampling was conducted at the normally designated sampling sites. No other sampling was conducted during the test. Figure 6b shows the sampler locations for both Runs 9 and 10.

Run 10: Run 10 was the final test of the series. All the testing parameters and sampling methods used in Run 9 were also followed in this run. The fire was extinguished in about 19 seconds, after a preburn duration of about 14 seconds. Eighty-eight pounds of HCFC 123 were used to extinguish the fire. The total amount of fuel used was 4.0 gallons. The FTIR (long angle) and Draeger sampling tubes were the only sampling conducted.

2. VOC Results (Summa® and Tenax®/Charcoal)

The following paragraphs include the detailed results of the Summa® and Tenax®/charcoal sampling efforts. The results of the volatile analyses from Summa®, Tenax®/charcoal, and FTIR sampling are summarized in Table 8; however, the majority of FTIR information is contained in subsection B.4. The upwind firefighter position always showed the lowest concentrations. The FTIR beam passed closest to the fire pit during most of the tests and showed the highest concentrations.

VOC results were obtained from four separate sampling locations for six different tests (Test Runs 1, 2, 4, 5, 6, and 7). The sampling locations utilized for these measurements were upwind to the training pit, in the firefighter's breathing area, in the fire plume, and downwind of the training pit. In addition, method and field blanks for the Summa® canisters and Tenax®/charcoal adsorbent traps were analyzed.

All of the test conditions for the Main Test used jet fuel (JP-4) for the test fire. The VOCs attributable to JP-4 consisted of a complex mixture of hydrocarbons (HCs), including alkanes, alkenes, and aromatics. Since the nonaromatic HCs are generally considered to be less of a health concern, only the aromatic compounds attributable to JP-4 (including benzene and toluene) were included as target analytes for quantitative determination.

Quantitative determination was performed on a number of target organic compounds selected prior to the Main Test. These target analytes were chosen based on the VOCs observed in the Screening Study (Halon 1211 only), a list of candidate VOCs provided by the Air Force, and compatibility with the analytical methods employed. In addition, a semiquantitative measure of the tentatively identified compounds (TICs) was provided by searching the analytical data files.

Example mass spectra of Halon 1211, HCFC 123, and PFH are given in Figure 7. Figure 8 shows reconstructed ion chromatograms (RICs) for the Summa® canister, with test Run 1 showing jet fuel only. A list of the analytes chosen for the Main Test is given in Table 9.

TABLE 8. MAIN TEST—SUMMARY RANGE OF VOLATILE EMISSIONS FROM
SUMMA®/TENAX®/CHARCOAL, AND FTIR (units are ppm, v/v).^a

Method	Compound	JP-4 only (Run 1)			Halon 1211 (Run 2)			HCFC 123 (Runs 4 and 5)			PFH (Runs 6 and 7)		
		FF	Plume	DW	FF	Plume	DW	FF	Plume	DW	FF	Plume	DW
Summa/ T/C	Halon 1211	0 - .0001	-	-	>.2 - 4	1.0 - 90	112	.025 - .044	.03 - 1.8	.1 - 1.8	0 - .01	.002 - .005	0 - .025
	HCFC 123	0	-	-	0 - .0002	0 - .003	-	>.2 - >5.4	>.2 - 180	>.17 - 129	.02 - .06 ^c	.002 - .08 ^c	.035 - .28
	PFH	0	-	-	0	0	-	0	0	0	.07 - .26	>.01 - .24	>.1 - .380
	Dichlorodifluoro- methane	0 - .001	.003	-	0 - .0016	.05 - .085	.031	.001 - .007	.012 - .26 ^c	.02 - .14	0 - .018	0 - .012	0
	Chloromethane	0 - .0002	-	-	0 - .0004	.13 - >.2.7	.03	0 - .0006	0 - >.0.4 ^b	.05 ^c - .10	0	>.32 - .54	0 - .007
	Dichlorofluoro- methane	0	-	-	.003 - .006	.006 - .08	.12	0	0 - .04	.003 - .02	0	0	0
	1,2-Dichloro- 1,1,2-trifluoro- ethane	0	-	-	0	-	-	.12 - .25	.1 - 16	25 ^b	0 - .009	0 - .005	.001 - .023
	Benzene	.001 - .06	1.0	-	.03	.18 - .44	.07	.004 - .06	.04 - .7 ^c	.04 - .35	.004 - .062	.013 - .1	.05 - .27
	Dibromomethane	0	-	-	0 - .00002	.045 - .07	-	0	0	0	0	0	0
	Toluene	.003 - .09	.076	.005	.038 - .05	.34 - .45	.25	.013 - .15	.1 - .46 ^c	.14 - 1.2	.007 - .15 ^c	.07 - .16 ^c	.19 - 1.2
	m- & p-Xylene	.0005 - .019	.012	-	.011 - .013	.07 - .12	.08	.0016 - .036	.02 - .1 ^c	.05 - .25	.002 ^c - .033 ^c	.012 - .018	.045 - .28
	o-Xylene	.0004 - .013	.009	-	.008 - .009	.06 - .07	.05	.0009 - .033	.013 - .06 ^c	.03 - .15	.002 ^c - .022 ^c	.007 - .014	.009 - .17
	Ethynylbenzene	.0002 - .006	.065	-	0 - .001	.02 - .19	-	0 - .007	.014 - .16	.002 - .04	.002 ^c	.007 ^c - .025	.007 - .009 ^c
	Styrene	.00006 - .005	.035	-	0 - .001	.015 - .025	-	.0001 ^c - .006	0 - .033 ^c	.004 ^c - .02	0 - .0007 ^c	.002 ^c - .005	.003 - .012 ^c
	1-Phenyl-1- propyne	.021	.021	.005	0 - .005	0	-	0 - .014	0 - 1.8	0 - .01 ^c	0 - .004	0	0 - .027
	4-Ethynyltoluene	0.00001 - .022	.056	.004	0 - .0006	0 - .003	-	0 - .021	0 - .008	0	0	0 - .002	0 - .02
	1,3-Butadiene	0	.028	-	a	.1 ^b	.1 ^b	0	0	0 - .06 ^b	0	.003 - .015	0 - .017
	Dibromofluoro- methane	0	-	-	0	0 - .0004	-	0	0	0	0	0	0
FTIR	Halon 1211	0	0	3400	4300	(Run 2)	(Run 3)	(Runs 4 & 5)	(Run 10)	(Runs 7 & 8)	(Run 9)		
	HCFC 123	0	0	-	-	-	-	1200-8200	5400	-	-		
	PFH	0	0	-	-	-	-	120 - 240	110	940 - 1400	870		
	HCl	0	0	30	80	42	30	0	0	0	0		
	HBr	0	0	42	140	24	24	0	0	0	0		
	HF	0	0	24	44	19	19	60 - 120	69	65-120	43		
	COF ₂	0	0	19	35	52	52	28 - 72	33	87-95	35		
	CO	6.5	6.5	220	140	220	220	52 - 180	69	79-110	44		
	JP-4	2.9	2.9	3	220	220	220	38 - 200	120	72-110	45		
	Acetylene	.26	.26	3	6	3	3	1 - 11	3	0 - 1	2		

^a Upwind results contained none of the target VOC analyses above MDLs.

^b Interference makes quantitation suspect.

^c Results from one sampling method have been ignored.

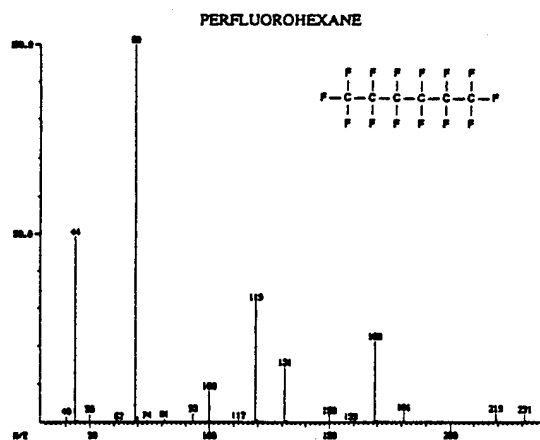
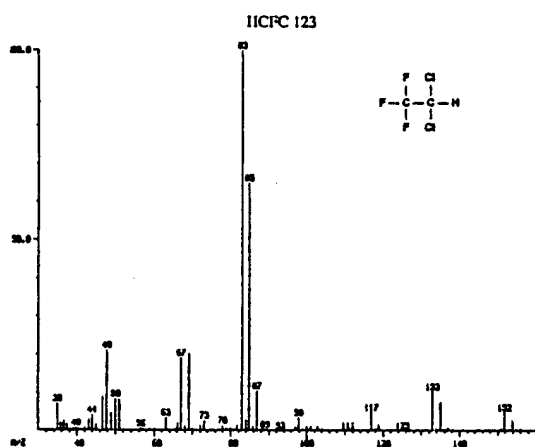
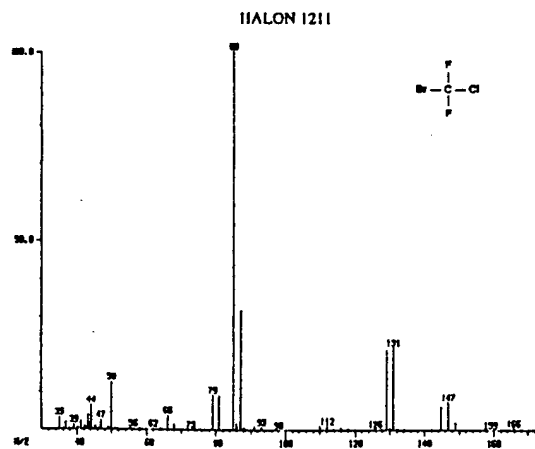


Figure 7. Example mass spectra of Halon 1211, HCFC 123, and PFH.

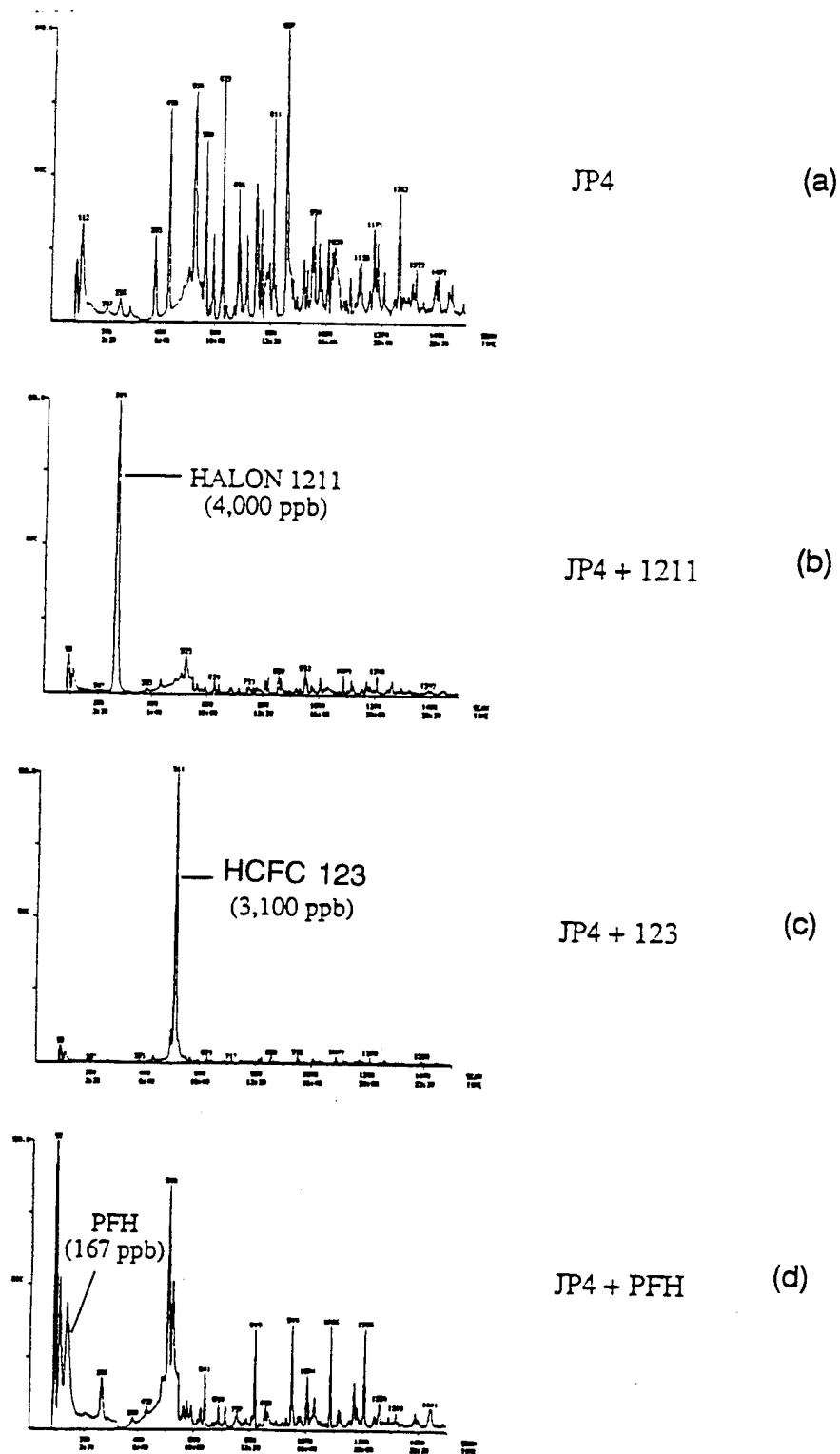


Figure 8. RICs for firefighter's breathing area VOCs from Summa® samples.

TABLE 9. VOCs DETECTED DURING MAIN TEST
FROM SUMMA® AND TENAX®/CHARCOAL.

Halon 1211
Perfluorohexane
HCFC 123
Dichlorodifluoromethane
Chloromethane
1,3-Butadiene
Dichlorofluoromethane
1,2-Dichloro-1,1,2-trifluoroethane
Dibromofluoromethane
Benzene
Dibromomethane
Toluene
m- and *p*-Xylene
Ethynylbenzene
o-Xylene
Styrene
1-Phenyl-1-propyne
4-Ethynyltoluene

The Summa[®] canister method provided a much wider quantitative concentration range than the adsorbent trap method because multiple analyses are possible from the same canister. The Summa[®] canister method provided a quantitative concentration range of 5 ppb to 300,000 ppb (by volume). The Tenax[®]/charcoal adsorbent trap method, on the other hand, achieved lower method detection limits (MDLs) and provided a quantitative concentration range of 0.3 ppb to 50 ppb. The MDLs and the concentration ranges attainable by Summa[®] canister and Tenax[®]/charcoal trap for each individual species are given in Table C-1 in Appendix C.

a. Firefighter's Breathing Area Results

Figure 8 shows RICs for the Summa[®] canister samples taken in the firefighter's breathing zone. The jet fuel-only test (Test Run 1, Figure 8) gives a RIC that shows a complex chromatogram made up of many hydrocarbon compounds. This jet-fuel chromatogram pattern, or "matrix," is evident in the results from all the remaining tests where extinguishing agents were used. Each respective test also shows a dominant compound in the RIC corresponding to the extinguishing agent utilized (Figure C-1 in Appendix C).

A summary of the target VOC analyte concentrations (ppb) for all samples collected in the firefighter's breathing zone is presented in Table 10. The ranges are determined for the Tenax[®]/charcoal traps, the Summa[®] canisters, and the Summa[®] canisters repeated at reduced sample volume.

The presence of Halon 1211 in the HCFC 123 and PFH tests is due to carryover from Halon 1211 in the fire extinguishers, which were not specially cleaned or purged of agent between tests. The same applies to HCFC 123 appearing in the PFH tests.

Several TICs were also identified and estimated concentrations are reported in Table C-2 in Appendix C. These compounds were primarily cyclic and aromatic hydrocarbons at low concentrations and low toxicity.

b. Plume Analytical Results

A summary of the plume concentration ranges for the target VOC analytes is given in Table 11. The ranges are determined from analytical results for the Tenax[®]/charcoal traps, the Summa[®] canisters, and the Summa[®] canisters repeated at reduced sample volume. Any TICs observed, and their respective concentrations, are summarized in Table C-3 in Appendix C. The list of TICs is more extensive for plume samples than for samples collected in the firefighter's breathing zone.

Figures C-2 and C-3 in Appendix C show example RICs for Summa[®] canister and Tenax[®]/charcoal adsorbent trap samples, respectively, collected in the plume for each test condition.

TABLE 10. MAIN TEST—SUMMARY OF TARGET VOC ANALYTE CONCENTRATIONS FOR ALL SAMPLES
COLLECTED IN FIREFIGHTER'S BREATHING ZONE (FROM SUMMA® AND TENAX®/CHARCOAL)
(Concentration, ppb).

Analyte	JP-4 (Run 1)	HALON 1211 (Run 2)	HCFC 123 (Runs 4 & 5)	PFH (Runs 6 & 7)
Halon 1211	0-13	>209-4000	24.7-44	0-96
HCFC 123	0	0-0.216	>199->5400	21.4-88**
PFH	0	0	0	69-26100
Dichlorodifluoromethane	0-1.06	0-1.62	0.97-7.3	0-17.6
Chloromethane	0-0.22	0-0.41	0-0.63	0
1,3-Butadiene	0	b	0	0
Dichlorofluoromethane	0	2.69-5.6	0	0
1,2-Dichloro-1,1,2-trifluoroethane	0	0	121-2520 ^d	0-9.2
Dibromofluoromethane	0	0	0	0
Benzene	1.24-59	27.2-27.7	3.7-63	3.5-62
Dibromomethane	0	0-0.022	0	0
Toluene	2.58-94	38-50	12.7-150 ^a	6.9-154*
<i>m</i> - and <i>p</i> -xylene	0.51-19.1	10.5-13.2	1.55-36	2.27**-33*
Ethynylbenzene	0.19-5.8	0-1.16	0-6.6	2.2**-2.4*
<i>o</i> -Xylene	0.35-12.8	7.5-9	0.89-33	1.56**-22.5*
Styrene	0.057-5.2	0-1.17	0.137**-6.5	0-0.74*
1-Phenyl-1-propyne	21.1°	0-5°	0-14.3	0-3.5°
4-Ethynyltoluene	0.088-22.1	0-0.57	0-21	0

^a Exceeds upper limit of T/C calibration curve.

^b Interference from high amounts of Halon 1211 makes quantitation suspect.

^c Interference from 1,2,3-trimethylbenzene makes quantitation suspect.

^d Interference from high amounts of HCFC 123 makes quantitation suspect.

* Ignored the higher level detected from 5-mL sample.

** Ignored ND results from Summa canisters®.

TABLE 11. MAIN TEST—SUMMARY OF TARGET VOC ANALYTE CONCENTRATIONS FOR SAMPLES COLLECTED IN PLUME (FROM SUMMA® AND TENAX®/CHARCOAL)
(Concentration, ppb).

Analyte	JP-4 ^a (Run 1)	HALON 1211 (Run 2)	HCFC 123 (Runs 4 & 5)	PFH (Runs 6 & 7)
Halon 1211	—	>1000-90000	30-1800	1.5-5
HCFC 123	—	0-3	>180-180000	2-80*
PFH	—	0	0	>100-24000
Dichlorodifluoromethane	3.4	50-85	12-260*	0-12
Chloromethane	—	130->2700 ^a	0->360 ^a	>320-540
1,3-Butadiene	25.5	100 ^b	0	3-15
Dichlorofluoromethane	—	6-82	0-40	0
1,2-Dichloro-1,1,2-trifluoroethane	—	—	>100-16000 ^d	0-5
Dibromofluoromethane	—	0-0.4	0	0
Benzene	1020	180-440	40-700*	13-100
Dibromomethane	—	45-70	0	0
Toluene	76	340-450	100-460*	70->175 ^a
<i>m</i> - and <i>p</i> -xylene	11.8	70-115	20-100*	12-18
Ethynylbenzene	65	20-190 ^a	14-160*	7**-25
<i>o</i> -Xylene	8.9	60-70	13-60	7-14
Styrene	35	15-25	0-33*	2**-5
1-Phenyl-1-propyne	21.4	0 ^c	0-1800 ^c	0 ^c
4-Ethynyltoluene	56	0-3	0-8	0-2

^a Exceeds upper limit of T/C calibration curve range.

^b Interference from Halon 1211 makes quantitation suspect.

^c Interference from 1,2,3-trimethylbenzene makes quantitation suspect.

^d Interference from HCFC 123 makes quantitation suspect.

^e Summa results only; vol. sampled data not available for T/C sample.

* Ignored the higher level detected from 5-mL Summa® sample.

** Ignored ND results from Summa® canisters..

c. Upwind and Downwind Analytical Results

The VOC samples collected at the upwind location contained none of the target analytes above MDLs, but the downwind VOC samples contained significant levels of the target analytes. In most cases, the extinguishing agent concentrations were higher in the downwind location than in the plume itself. This is not surprising since the physical process of putting out the fire displaces the plume from the plume-sampling probe.

A summary of the concentration ranges for the target analytes found in the downwind location is given in Table 12. The ranges were determined from analytical results for the Tenax[®]/charcoal adsorbent traps, the Summa[®] canisters, and the Summa[®] canister repeated at a reduced sample volume.

The TICs observed for each test condition, along with their semiquantitative concentrations are given in Table C-4 in Appendix C.

3. Semivolatile Organics and Dioxins/Furans Results

The following paragraphs include the results of PUF sample collection (followed by extraction and GC/MS analysis) for SVOCs and PCDDs/PCDFs. The semivolatile analyses are summarized in Table 13, and the PCDD/PCDF analyses are summarized in Table 14.

SVOC and PCDD/PCDF results were obtained from four sampling locations for six different test runs (Runs 1, 2, 4, 5, 6, and 7). The sampling locations utilized for these measurements were upwind of the training pit, in the firefighter's breathing area, in the fire plume, and downwind of the training pit.

Particulate mass measurements of the PUF filter catch were attempted, but showed negative weights during extinguisher agent application due to reaction of HF with silica in the filters to produce volatile SF₄. During Run 1, no extinguisher agent was applied, allowing particulate mass measurements to be calculated. The results of Run 1 are: plume 42 mg/m³; downwind 1 mg/m³; FF 0.8 mg/m³. Particulate results are included in Table C-5.

Quantitative determination was performed on a number of target SVO analytes selected prior to the Main Test. These targets were chosen based on the SVOs observed in the Screening Study (Halon 1211 only), a list of candidate SVOs provided by the Air Force, and compatibility with the analytical methods employed. Table A-9 contains the SVOC target analytes for this study. Quantitative determination was provided for all the 2,3,7,8-substituted PCDD/PCDFs as well as total tetra- through octa-PCDD/PCDFs by homolog group. In addition, a semiquantitative measure of the TICs was provided by searching the analytical data files after the initial analysis.

TABLE 12. MAIN TEST—SUMMARY OF TARGET VOC ANALYTE CONCENTRATIONS FOR SAMPLES
COLLECTED DOWNWIND (FROM SUMMA® AND TENAX®/CHARCOAL)
(Concentration, ppb).

Analyte	JP-4 ^a (Run 1)	HALON 1211 (Run 2)	HCFC 123 (Runs 4 & 5)	PFH (Runs 6 & 7)
Halon 1211	-	112,000	100 to 1,800	0 to 25
HCFC 123	-	-	>170 to 129,000	35 to 280
PFH	-	-	0	> 96 to 380,000 ^a
Dichlorodifluoromethane	-	31	20 to 135	0
Chloromethane	-	30	50** to 100	0 to 7
1,3-Butadiene	-	103 ^b	0 to 55 ^b	0 to 17
Dichlorofluoromethane	-	120	3 to 20	0
1,2-Dichloro-1,1,2-trifluoroethane	-	-	25,000 ^d	1 to 23
Dibromofluoromethane	-	-	0	0
Benzene	-	69	40 to 350	50 to 270
Dibromomethane	-	-	0	0
Toluene	4.9	250	140 to 1,200	190 to 1,220
<i>m</i> - and <i>p</i> -xylene	-	77	50 to 250	45 to 280
Ethynylbenzene	-	-	2 to 40	7** to 9*
<i>o</i> -Xylene	-	46	30 to 150	9 to 170
Styrene	-	-	4.** to 20	3 to 12*
1-Phenyl-1-propyne	4.5	-	0 to 10 ^c	0 to 27
4-Ethynyltoluene	3.6	-	0	0 to 20

^a Exceeds upper limit of T/C calibration curve.

^b Interference from Halon 1211 makes quantitation suspect.

^c Interference from 1,2,3-trimethylbenzene makes quantitation suspect.

^d Interference from HCFC 123 makes quantitation suspect.

^e Summa® results only; T/C sample lost during analysis.

* Ignored the higher level detected from 5-mL Summa® sample.

** Ignored ND results from Summa canisters®.

TABLE 13. MAIN TEST—SUMMARY OF SVOC EMISSIONS FROM PUF CARTRIDGES* (units are $\mu\text{g}/\text{m}^3$).

Compound	JP-4 only (Run 1)			Halon 1211 (Run 2)			HCFC 123 (Runs 4 & 5)			PFH (Runs 6 & 7)		
	FF	Plume	DW	FF	Plume	DW	FF	Plume	DW	FF	Plume	DW
Phenol	9.5	2.8	109	<0.8	4.0	<1.3	<0.9	12 - 16	41	<0.9	<1	<0.9
Acenaphthene	-	1.7	-	<0.8	-	<1.3	-	<1.2	<1.3	<1	<0.8	<1.7
Acenaphthylene	-	120	-	-	9.5	<1.3	<0.9	<1.3-21	<1.3	<1	2.2 - 7.2	<1.7
Anthracene	-	9.3	-	-	-	-	-	<1.2	-	-	<1.4	<1.7
Benz[a]anthracene	-	11	-	-	1.8	-	-	8.5	-	-	-	-
Benzo[a]pyrene	-	11	-	-	-	-	-	4.2	-	-	-	-
Benzo[b]fluoranthene	-	-	-	-	5.7	-	-	12	-	-	-	-
Benzo[k]fluoranthene	-	15	-	-	5.1	-	-	<1.2	-	-	-	-
Benzo[g,h,i]perylene	-	5.6	-	-	-	-	-	3.6	-	-	-	-
Chrysene	-	9.9	-	-	-	-	-	3.2	-	-	-	-
Fluoranthene	-	64	-	<0.8	25	<1.3	<0.9	1.3 - 52	<1.3	-	0.9 - 3.4	<1.3
Fluorene	-	17	-	<0.8	4.1	<1.3	-	1.3 - 7.3	-	-	0.84	<1.3
Indeno[1,2,3-cd]pyrene	-	6.7	-	-	-	-	-	<1.2 - 1.3	-	-	1.4	-
Naphthalene	<1.9	110	<5.8	1.1	120	4.0	1.8	4.8 - 170	6.7 - 13	<1 - 1.1	7.8 - 20	3.2 - 13
Phenanthrene	-	60	-	0.8	16	<1.3	<0.9	1.6 - 64	1.9 - 2.1	-	4.6 - 4.7	<1.7
Pyrene	-	35	-	<0.8	5.5	-	-	<1.3 - 18	-	-	2.1	<1.3
1-Methylnaphthalene	<1.9	6.6	<5.8	2.6	22	19	2.6	14	1.5 - 19	<1 - 2.6	6.9 - 11	15 - 90
Biphenyl	-	14	-	<0.8	17	2.9	<0.9	<1.3 - 21	3.6 - 5.0	<0.9	1.4 - 2.9	2.4 - 7.2
1-Phenylnaphthalene	-	1.9	-	-	-	-	-	1.3	-	-	-	-
1,3-Dimethylnaphthalene	-	2.2	-	<0.8	6.2	10	<0.9	<1.3 - 4.0	6.2 - 9.3	<1 - 0.9	2.3 - 4.0	7.9 - 39
1,2-Dimethylnaphthalene	-	-	-	-	<1.7	<1.3	-	-	<1.3	-	-	2.2
2-Vinylnaphthalene	-	7.9	-	-	0.15	-	-	1.6	-	-	<1.4	1.4
2,3,7,8-TCDF	-	-	-	-	-	-	-	-	-	-	-	-
1,2,3,7,8-PeCDF	-	-	-	-	-	-	-	0.08	0.037-0.038	-	-	-
2,3,4,7,8-PeCDF	-	-	-	-	-	-	-	0.130	0.064	-	0.063	-
1,2,3,4,6,7,8-HpCDF	-	-	-	-	-	-	0.005	-	-	-	-	-
1,2,3,4,7,8,9-HpCDF	-	-	-	-	-	-	-	2.3	-	-	-	-
1,2,3,4,6,7,8-HpCDD	-	-	-	-	-	-	-	0.15	-	-	-	-
1,2,3,4,6,7,8,9-OCDF	-	-	-	-	-	-	-	0.7 - 7.4	0.4 - 0.6	-	-	-
TCDF	-	-	-	-	0.64	-	-	0.5 - 3.3	0.4 - 0.8	-	0.068	-
PeCDF	-	-	-	-	0.87	-	-	0.87	0.5 - 0.6	-	0.33	-
PeCDD	-	-	-	-	-	-	-	0.007	-	-	-	-
HxCDF	-	-	-	-	-	-	-	0.3 - 9.2	0.2 - 0.3	-	-	-
HpCDF	-	-	-	-	-	-	-	2.5	-	-	-	-
HpCDD	-	-	-	-	-	-	-	0.15	-	-	-	-

* Upwind results contained none of the target SVOC analytes above MDLs.

TABLE 14. MAIN TEST—SVOC ANALYSIS RESULTS FOR THE FIREFIGHTER'S BREATHING AREA FROM PUF CARTRIDGES
(Runs 1 to 7; results reported in total $\mu\text{g}/\text{m}^3$ ^a).

No.	Target compound	Run 1 JP-4 C + F	Run 2 Halon 1211 C + F	Run 4 HCFC 123 C + F	Run 5 HCFC 123 C + F	Run 6 PFH C + F	Run 7 PFH C + F
9	Phenol	9.51	< 0.8	—	< 0.9	< 1	< 0.9
10	Acenaphthene	—	< 0.8	—	—	< 1	—
11	Acenaphthylene	—	—	—	< 0.9	< 1	—
12	Anthracene	—	—	—	—	—	—
13	Benz[a]anthracene	—	—	—	—	—	—
14	Benzo[a]pyrene	—	—	—	—	—	—
15	Benzo[b]fluoranthene	—	—	—	—	—	—
16	Benzo[k]fluoranthene	—	—	—	—	—	—
17	Benzo[g,h,i]perylene	—	—	—	—	—	—
18	Chrysene	—	—	—	—	—	—
19	Dibenz[a,h]anthracene	—	—	—	—	—	—
20	Fluoranthene	—	< 0.8	—	< 0.9	—	—
21	Fluorene	—	< 0.8	—	—	—	—
22	Indeno[1,2,3-cd]pyrene	—	—	—	—	—	—
23	Naphthalene	< 1.9	1.1	< 0.8	1.79	< 1	1.09
24	Phenanthrene	—	0.82	—	< 0.9	—	—
25	Pyrene	—	< 0.8	—	—	—	—
27	1-Methylnaphthalene	< 1.9	2.55	—	2.57	< 1	2.56
29	Biphenyl	—	< 0.8	—	< 0.9	< 1	< 0.9
30	1-Phenylnaphthalene	—	—	—	—	—	—
33	1,3-Dimethylnaphthalene	—	< 0.8	—	< 0.9	< 1	0.93
34	1,2-Dimethylnaphthalene	—	—	—	—	—	—
35	2-Vinylnaphthalene	—	—	—	—	—	—
Surrogates (% recovery)							
1	d ₅ -Nitrobenzene	42.2	58.0	28.0	28.0	27.0	22
2	d ₄ -1,2-Dichlorobenzene	15.1	22.0	6.4	7.7	9.2	5.38
3	d ₁₄ -Terphenyl	96.0	104	82.5	79.7	63.8	71.5
Lab code		27951	27953	27955	27957	27959	27961
GC/MS file (6207...)		K21W2	K21W4	K21W6	K21W7	K21W8	K22W4
Date sampled							
Date analyzed		21 Nov 91	21 Nov 91	21 Nov 91	21 Nov 91	21 Nov 91	22 Nov 91

^a Sample split factor = 2, final sample extract volume = 100 μL .

C = cartridge, F = filter, R = probe rinse

(—) = not detected

< = detected but less than X $\mu\text{g}/\text{m}^3$

Separate filters and probe rinse samples were collected for analysis. In addition, blank filters and cartridges were included for analysis.

a. Analytical Considerations

All of the test conditions in the Main Test used jet fuel (JP-4) for test fire. The SVOs attributable to JP-4 consist of the complex mixture of hydrocarbons, including phenol and polyaromatic hydrocarbons (PAHs). Almost all of the SVO target analytes chosen for this study originate from the JP-4 fuel. Concentration ranges from $0.8 \mu\text{g}/\text{m}^3$ to $120 \mu\text{g}/\text{m}^3$ were seen for the SVOs, and from $4 \text{ pg}/\text{m}^3$ to $20 \text{ pg}/\text{m}^3$ were seen for the PCDDs/PCDFs.

b. Firefighter's Breathing Area Results

(1) SVO Results. The jet fuel-only chromatogram (Figure 9, Run 1) gives a complex chromatogram made up of many compounds, including the surrogate compounds added to the sample prior to extraction. In fact, all of the samples for the various test conditions give a similar RIC, indicating that the predominant SVOs come from the JP-4 used for the fire.

Table 14 contains a summary of the SVO target analyte concentrations for samples collected from the firefighter's breathing area. Very few SVOs were observed for these test conditions, but phenol indicated the highest concentration at $9.5 \mu\text{g}/\text{m}^3$ in Run 1 using only JP-4. The remainder of the target SVOs for the firefighter's breathing area are near or below the MDL. The TICs observed for PUF samples, along with their semiquantitative concentrations, are given in Table C-6 in Appendix C.

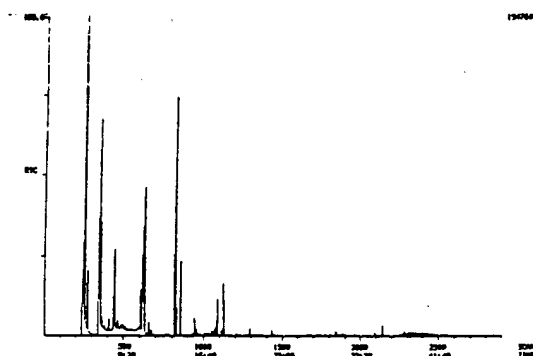
(2) PCDD/PCDF Results. Only 1,2,3,4,6,7,8-heptachlorodibenzofuran was detected during Run 5 at approximately $5 \text{ pg}/\text{m}^3$. No other PCDD/PCDF isomer was detected for samples collected from the firefighter's breathing area. The analytical methods used give results for both isomer-specific (the 2,3,7,8-substituted position) PCDD/PCDFs, as well as total PCDD/PCDFs by homolog group (tetra- through octa-chlorine substitution). All of the 2,3,7,8-substituted isomers of PCDDs and PCDFs were included in the calibration of the GC/MS system to provide quantitative concentrations. The other PCDD/PCDF isomers were quantitated collectively, along with other isomers within a homolog group, to yield total tetra- through octa-chlorinated dibenzodioxin/furans.

c. Plume Analytical Results

(1) SVO Results. A summary of the target SVO analyte concentrations is given in Table 15. In general, most of the target SVOs for these test conditions were present at various levels of concentration. Note that most of the target SVOs detected appear to be attributable to JP-4 fuel products of complete and incomplete combustion. For both the HCFC 123 and PFH agents, the range of concentrations is obtained

Run # 1

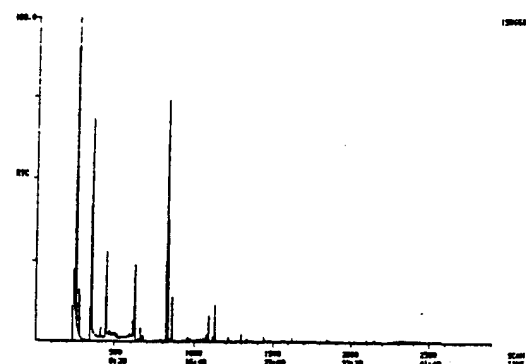
(a)



JP4

Run # 2

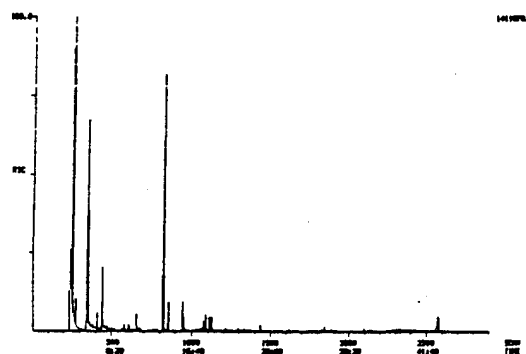
(b)



JP4 + 1211

Run # 4

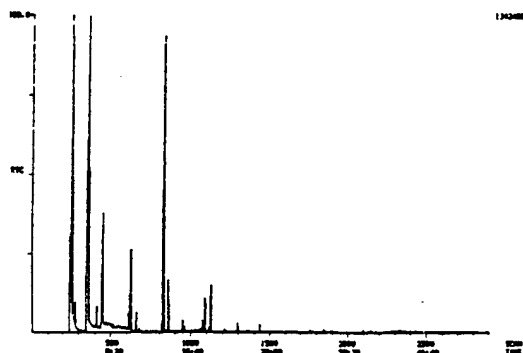
(c)



JP4 + 123

Run # 6

(d)



JP4 + PFH

Figure 9. RICs for firefighter's breathing area SVOs from PUF samples for Main Test.

TABLE 15. MAIN TEST—SVOC ANALYSIS RESULTS FOR THE PLUME
FROM PUF CARTRIDGES
(Results reported in total $\mu\text{g}/\text{m}^3$ ^a).

No.	Target compound	Run 1	Run 2	Run 4	Run 5	Run 6	Run 7
		JP-4	Halon 1211	HCFC 123	HCFC 123	PFH	PFH
		C + F + R	C + F + R	C + F + R	C + F + R	C + F + R	C + F + R
9	Phenol	2.84	4.00	15.7	11.6	3.03	2.67
10	Acenaphthene	1.72	—	< 1.2	—	—	< 0.8
11	Acenaphthylene	120 ^b	9.54	21.1	< 1.3	7.20	2.15
12	Anthracene	9.32	—	< 1.2	—	< 1.4	—
13	Benz[a]anthracene	10.8	1.76	8.51	—	—	—
14	Benzo[a]pyrene	10.6	—	4.16	—	—	—
15	Benzo[b]fluoranthene	—	5.68	12.2	—	—	—
16	Benzo[k]fluoranthene	15.2	5.13	< 1.2	—	—	—
17	Benzo[g,h,i]perylene	5.58	—	3.64	—	—	—
18	Chrysene	9.93	—	3.18	—	—	—
19	Dibenz[a,h]anthracene	—	—	< 1.2	—	—	—
20	Fluoranthene	64.0 ^b	24.8	51.6 ^b	1.3	3.40	0.92
21	Fluorene	16.7	4.12	7.34	1.3	—	0.84
22	Indeno[1,2,3-cd]pyrene	6.70	—	< 1.2	1.3	< 1.4	—
23	Naphthalene	110 ^b	120	172 ^b	4.78	20.3	7.84
24	Phenanthrene	60.2 ^b	16.0	63.6 ^b	1.56	4.63	4.70
25	Pyrene	35.4	5.54	17.6	< 1.3	2.11	< 0.8
27	1-Methylnaphthalene	6.60	21.9	14.2	—	10.8	6.89
29	Biphenyl	14.3	17.3	20.7	< 1.3	2.92	1.43
30	1-Phenylnaphthalene	1.88	—	1.32	—	—	—
33	1,3-Dimethylnaphthalene	2.19	6.24	4.02	< 1.3	3.98	2.29
34	1,2-Dimethylnaphthalene	—	—	—	—	—	—
35	2-Vinylnaphthalene	7.90	< 1.7	1.56	—	< 1.4	—
Surrogates (% recovery)							
1	d ₅ -Nitrobenzene	30.8	—	7.53	46.2	35.2	97.2
2	d ₄ -1,2-Dichlorobenzene	7.83	23.6	20.0	20.0	9.20	27.8
3	d ₄ -Terphenyl	59.5	64.5	65.2	71.5	57.2	150
Lab code		27963	27964	27965	27966	27967	27968
GC/MS File (6207...)		K22W12	K22W11	K22W10	K22W5	K22W7	K22W2
Date sampled							
Date analyzed		22 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91

^a Sample split factor = 2, final sample extract volume = 100 μL .

^b Results are from an analysis of a dilution of the original analyzed sample.

C = Cartridge, F = filter, R = probe rinse.

(-) = Not detected.

< = Detected but less than X $\mu\text{g}/\text{m}^3$.

from the combined results of the initial and repeated test. A list of TICs is given in Table C-7 in Appendix C, and example RICs are in Figure C-4.

(2) PCDD/PCDF Results. A summary of the PCDD/PCDF concentrations (pg/m^3) from plume samples is given in Table 16. For both the HCFC 123 and PFH agents, the concentration range is obtained from the combined results of the initial and repeated test run. Of particular interest is the fact that while no PCDDs/PCDFs are generated from JP-4 only (Run 1), formation of PCDD/PCDFs during the combustion of extinguishing agents did occur. A closer examination of the results show that mostly PCDFs are produced, and PFH produces the fewest PCDFs compared to HCFC 123 and Halon 1211.

d. Upwind and Downwind Analytical Results—SVOs and PCDD/PCDFs

SVOC and PCDD/PCDF samples collected at the upwind location contained none of the target analytes above MDLs.

(1) SVO Results. A summary of the target SVO analyte concentrations ($\mu\text{g/m}^3$) for all downwind samples is presented in Table 17. In general, most of the target SVOs for these test conditions were detected at varying concentration levels. Most of the target SVOs detected can be attributed to JP-4 products of complete and incomplete combustion. Example RICs are shown in Figure C-5 in Appendix C, and TICs are shown in Table C-8.

(2) PCDD/PCDF Results. A summary of the PCDD/PCDF concentrations (pg/m^3) from the downwind location is given in Table 18. Again, note that while no PCDDs/PCDFs were generated from JP-4 only (Test 1), formation of PCDDs/PCDFs during the combustion of extinguishing agents was observed in the HCFC 123 test runs. A closer examination of the results shows that only PCDFs are detected from the HCFC 123 test run.

4. FTIR Volatile Toxic Gases Results

The following paragraphs include the results of FTIR sampling for the volatile toxic gases. The toxic gases included for discussion are: hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen bromide (HBr), carbonyl fluoride (COF_2), carbon monoxide (CO), and acetylene (Acet). The fuel JP-4 was used as a reference, and information regarding emissions from it is also reported.

Results for volatile toxic gases were obtained from sampling the plume for different test runs (Runs 1 through 5 and 7 through 10).

TABLE 16. MAIN TEST—PCDD/PCDF RESULTS FOR THE PLUME FROM PUF CARTRIDGES
(pg/m³).

Target analyte	Run 1 JP-4	Run 2 Halon 1211	Run 4 HCFC 123	Run 5 HCFC 123	Run 6 PFH	Run 7 PFH
<u>2,3,7,8-Substituted isomer</u>						
2,3,7,8-TCDF	-	148	-	-	-	-
2,3,7,8-TCDD	-	-	-	-	-	-
1,2,3,7,8-PeCDF	-	-	-	79.8	-	-
2,3,4,7,8-PeCDF	-	-	-	129	63.4	-
1,2,3,7,8-PeCDD	-	-	< 2.99	-	-	-
1,2,3,4,7,8-HxCDF	-	-	-	-	-	-
1,2,3,6,7,8-HxCDF	-	-	-	-	-	-
2,3,4,6,7,8-HxCDF	-	-	-	-	-	-
1,2,3,7,8,9-HxCDF	-	-	-	-	-	-
1,2,3,4,7,8-HxCDD	-	-	-	-	-	-
1,2,3,6,7,8-HxCDD	-	-	-	-	-	-
1,2,3,7,8,9-HxCDD	-	-	-	-	-	-
1,2,3,4,6,7,8-HpCDF	-	-	< 7.48	< 11.9	< 8.44	-
1,2,3,4,7,8,9-HpCDF	-	-	2275	-	-	-
1,2,3,4,6,7,8-HpCDD	-	-	148	-	-	-
1,2,3,4,6,7,8,9-OCDF	-	-	7425	670	-	-
1,2,3,4,6,7,8,9-OCDD	-	-	-	-	-	-
<u>Homolog group</u>						
TCDF	-	638	3341	477	68.2	-
TCDD	-	-	-	-	-	-
PeCDF	-	872	-	867	327	-
PeCDD	-	-	6.77	-	-	-
HxCDF	-	-	9221	311	-	-
HxCDD	-	-	-	-	-	-
HpCDF	-	-	2503	-	-	-
HpCDD	-	-	148	-	-	-

Table 17. MAIN TEST—SVOC ANALYSIS RESULTS FOR DOWNWIND
SAMPLING FROM PUF CARTRIDGES*
(Results reported in total $\mu\text{g}/\text{m}^3$ ^a).

No.	Target compound	Run 1	Run 2	Run 4	Run 5	Run 6	Run 7
		JP-4 C + F + R	Halon 1211 C + F + R	HCFC 123 C + F + R	HCFC 123 C + F + R	PFH C + F + R	PFH C + F + R
9	Phenol	109	< 1.3	—	41.0	2.99	5.21
10	Acenaphthene	—	< 1.3	—	< 1.3	< 1.7	—
11	Acenaphthylene	—	< 1.3	< 1.3	< 1.3	< 1.7	< 1.3
12	Anthracene	—	—	—	—	< 1.7	—
13	Benz[a]anthracene	—	—	—	—	—	—
14	Benzo[a]pyrene	—	—	—	—	—	—
15	Benzo[b]fluoranthene	—	—	—	—	—	—
16	Benzo[k]fluoranthene	—	—	—	—	—	—
17	Benzo[g,h,i]perylene	—	—	—	—	—	—
18	Chrysene	—	—	—	—	—	—
19	Dibenz[a,h]anthracene	—	—	—	—	—	—
20	Fluoranthene	—	< 1.3	< 1.3	< 1.3	—	< 1.3
21	Fluorene	—	< 1.3	—	—	—	< 1.3
22	Indeno[1,2,3-cd]pyrene	—	—	—	—	—	—
23	Naphthalene	< 5.8	4.03	6.74	13.0	3.2	12.6
24	Phenanthrene	—	< 1.3	2.08	1.87	< 1.7	< 1.3
25	Pyrene	—	—	—	—	—	< 1.3
27	1-Methylnaphthalene	< 5.8	19.4	19.3	1.47	14.9	90.0 ^b
29	Biphenyl	—	2.85	4.96	3.57	2.39	7.20
30	1-Phenylnaphthalene	—	—	—	—	—	—
33	1,3-Dimethylnaphthalene	—	10.4	9.27	6.17	7.85	38.6 ^b
34	1,2-Dimethylnaphthalene	—	< 1.3	< 1.3	< 1.3	—	2.16
35	2-Vinylnaphthalene	—	< 1.3	—	—	—	1.41
Surrogates (% recovery)							
1	d ₅ -Nitrobenzene	50.8	28.5	37.2	54.5	42.5	39.0
2	d ₄ -1,2-Dichlorobenzene	20.8	6.30	20.7	25.4	15.3	7.25
3	d ₁₀ -Terphenyl	95.0	104	81.8	72.0	77.5	70.2
Lab code		27952	27954	27956	27958	27960	27962
GC/MS File (6207...)		K21W3	K21W5	K22W6	K22W8	K22W3	K22W9
Date sampled							
Date analyzed		21 Nov 91	21 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91

^a Sample split factor = 2, final sample extract volume = 100 μL .

^b Results are from an analysis of a dilution of the original analyzed sample.

C = Cartridge, F = filter, R = probe rinse.

(—) = Not detected.

< = Detected but less than X $\mu\text{g}/\text{m}^3$.

* Upwind samples contained none of the target SVOC analytes above MDLs.

TABLE 18. MAIN TEST—PCDD/PCDF RESULTS FOR DOWNWIND SAMPLING*
FROM PUF CARTRIDGES (pg/m³).

Target analyte	Run 1 JP-4	Run 2 Halon 1211	Run 4 HCFC 123	Run 5 HCFC 123	Run 6 PFH	Run 7 PFH
<u>2,3,7,8-Substituted isomer</u>						
2,3,7,8-TCDF	-	-	< 3.27	-	-	-
2,3,7,8-TCDD	-	-	-	-	-	-
1,2,3,7,8-PeCDF	-	-	37.6	36.9	-	-
2,3,4,7,8-PeCDF	-	-	63.5	-	-	-
1,2,3,7,8-PeCDD	-	-	-	-	-	-
1,2,3,4,7,8-HxCDF	-	-	-	-	-	-
1,2,3,6,7,8-HxCDF	-	-	-	-	-	-
2,3,4,6,7,8-HxCDF	-	-	-	-	-	-
1,2,3,7,8,9-HxCDF	-	-	-	-	-	-
1,2,3,4,7,8-HxCDD	-	-	-	-	-	-
1,2,3,6,7,8-HxCDD	-	-	-	-	-	-
1,2,3,7,8,9-HxCDD	-	-	-	-	-	-
1,2,3,4,6,7,8-HpCDF	-	-	< 8.17	< 8.33	-	-
1,2,3,4,7,8,9-HpCDF	-	-	-	-	-	-
1,2,3,4,6,7,8-HpCDD	-	-	-	-	-	-
1,2,3,4,6,7,8,9-OCDF	-	-	601	390	-	-
1,2,3,4,6,7,8,9-OCDD	-	-	-	-	-	-
<u>Homolog group</u>						
TCDF	-	-	758	432	-	-
TCDD	-	-	-	-	-	-
PeCDF	-	-	497	567	-	-
PeCDD	-	-	-	-	-	-
HxCDF	-	-	176	304	-	-
HxCDD	-	-	-	-	-	-
HpCDF	-	-	-	-	-	-
HpCDD	-	-	-	-	-	-

Quantitation concentration range (5 to 25 pg/m³).

* Upwind results contained none of the target PCDD/PCDF analytes above the MDLs.

The FTIR is the only method that easily showed how the various gas concentrations changed during the brief test runs. The FTIR beam was positioned so that it could scan the plume near the fire zone during regular-angle settings; it scanned from several meters downwind of the fire during long-angle settings. The FTIR data show that the highest toxic compound concentrations occurred during the application of fire extinguishing agent. This implies that results from the other integrated sample methods should be corrected to reflect this. In other words, the relatively low concentrations integrated over the approximately 20 minutes of sampler running time should be adjusted as if the entire exposure occurred only during fire extinguishing agent application. This is referred to as "worst-case" data on Table 20 and in subsequent sections.

Tables 19 and 20 summarize the FTIR results. Table 19 is divided by fire phase, and Table 20 shows the highest 1-minute reading, equivalent worst-case concentration, and emission rate. Figure 10 shows an example FTIR concentration plot. The FTIR data in graphical form are included in Appendix C, in Figures C-6 through C-14. Separate left (L) and right (R) axes are used for the different compounds in order to clearly emphasize the time correlation of the concentrations. Traces of the infrared signatures of methane, benzene, and toluene were also seen, but only in the most intense spectra and not enough to quantify. Approximately 1 percent of the respective agents were converted to acid gases in these tests.

In nearly every case, emissions were higher during agent application than during the fire only phase. Due to the wider dispersal of agent in fighting the three-dimensional fires, the postfire concentrations were somewhat higher than during the Screening Test, but most of the emissions still occurred during agent application. This can be seen in the FTIR graphs found in Appendix C and the fire phase Table 20.

The concentrations reported by FTIR are probably lower than actual concentrations for several reasons. First, no corrections for temperature or pressure have been applied. The high test elevation (5000 feet above sea level) and the hot smoke plume both cause increases in concentration when corrected to standard conditions. Second, the beam length within the plume is uncertain because of turbulence, but the measured concentrations are an average across the smoke plume. Near the plume center, concentrations are higher than the average. Third, the hot plume causes the various compounds present to emit infrared at their characteristic wavelengths. Since the data were being calculated in absorbance mode, any infrared emissions will partially cancel the absorbance readings. Of the three factors above, only the pressure correction effect is known—about 20 percent. The other factors are probably similar in magnitude, so that the combined error could show true concentrations as much as double those reported.

TABLE 19. FTIR DATA BY FIRE PHASE
(Concentrations, ppm [v/v]).

Run Number	1 (R)	2 (R)	3 (L)	4 (R)	5 (R)	7 (R)	8 (R)	9 (L)	10 (L)
	JP-4	Halon 1211	Halon 1211	HCFC 123	HCFC 123	PFH	PFH	PFH	HCFC 123
Fuel	0.0	0.0	0.0	b	0.0	0.0	0.0	0.0	0.0
Fire	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Agent	4300	4300	3400	1200	8200	940	1400	870	5400
Out*	570	570	220	62	1700	940	730	600	1800
H	0.0	0.0	0.0	b	0.0	0.0	0.0	0.0	0.0
C	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
I	80	80	30	120	240	0.0	0.0	0.0	110
Out*	0.05	0.05	0.79	1.1	17	0.0	0.0	0.0	16
Fuel	0.0	0.0	0.0	b	0.0	0.0	0.0	0.0	0.11
Fire	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Agent	44	44	24	60	120	65	120	43	69
Out*	2.5	2.5	1.6	1.0	15	11	7.9	10	16
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
r	140	140	42	0.62	0.0	0.0	0.0	0.0	0.0
Out*	0.0	0.0	0.62	0.0	0.0	0.0	0.0	0.0	0.0
C	0.0	0.0	0.0	b	0.0	0.0	0.0	0.0	0.0
O	0.0	0.0	0.0	0.0	0.58	0.0	0.0	0.0	0.0
F	35	35	19	26	72	87	95	35	33
2	0.76	0.76	0.55	0.0	2.2	9.6	5.6	5.4	4.5
Fuel	0.0	24	2.1	b	0.0	0.0	0.0	1.4	0.0
Fire	6.5	33	1.6	0.0	0.0	0.0	6.2	3.8	0.0
Agent	140	140	52	52	180	79	110	44	69
Out*	0.0	22	7.2	16	20	9.7	5.2	11	14
J*	3.7	140	0.23	b	2.1	50	6.9	3.6	0.0
P	2.9	23	4.5	50	15	56	37	3.6	0.66
4	7.1	220	220	38	200	110	72	45	120
Out*	29	29	27	0.83	38	40	20	11	54
A*	0.0	1.1	0.07	b	0.0	0.14	0.06	0.0	0.0
C	0.26	0.7	0.07	0.11	0.0	0.23	0.28	0.0	0.0
E	6.4	6.4	3.10	1.4	11	0.0	0.29	0.86	2.9
T	0.0	0.85	0.25	0.49	0.96	1.10	0.0	2	0.37

* Fire was not extinguished in Runs 1, 2 and 4.

b FTIR began recording when the fire started.

c Acetylene.

* Based on molecular weight of undecane.

L = Long-angle path (just slightly downwind of plume).
R = Regular-angle path (directly through the plume).

TABLE 20. FTIR SUMMARY DATA WITH HIGHEST 1-MINUTE READING
(Concentration, ppm [v/v]).

Run Number	1 (R)	2 (R)	3 (L)	4 (R)	5 (R)	7 (R)	8 (R)	9 (L)	10 (L)
	JP-4	Halon 1211	Halon 1211	HCFC 123	HCFC 123	PFH	PFH	PFH	HCFC 123
1 min maximum									
Avg. conc. worst case		4,300	3,000	1,100	5,600	1,900	1,000	900	3,400
Mass (g)/kg agent		2,900	2,500	350	23,000	11,000	1,900	1,700	6,200
Total mass (g)		1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Agent		68,000	29,000	59,000	45,000	30,000	40,000	45,000	40,000
H		72	25	120	150				56
C		36	20	32	370				97
I		2.7	1.8	22	3.8				3.7
Total mass (g)		180	52	1,300	170				150
1 min maximum									
Avg. conc. worst case		41	21	59	77	47	66	29	40
Mass (g)/kg agent		24	18	17	240	170	120	52	71
Total mass (g)		0.99	0.86	6.2	1.4	0.9	3.7	1.8	1.5
H		68	25	370	62	27	150	80	60
B		130	34						
r		64	27						
Total mass (g)		11	5.2						
1 min maximum		720	150						
1 min maximum									
Avg. conc. worst case		32	16	26	40	52	50	22	17
Mass (g)/kg agent		17	12	7.1	83	160	93	36	29
Total mass (g)		2.3	2	8.7	1.5	2.9	9.4	4.1	2
1 min maximum		160	59	510	69	87	370	190	81
30		130	45	51	110	49	61	30	38
9.4		120	49	23	350	160	110	55	67
Mass (g)/kg agent		7.1	3.3	12	2.8	1.2	4.8	2.6	2
Total mass (g)		480	97	720	120	36	190	120	79
1 min maximum									
Avg. conc. worst case		210	190	79	130	100	55	30	84
Mass (g)/kg agent		190	190	26	550	630	110	58	160
Total mass (g)		62	70	75	24	9.4	26	15	26
4		4200	2,100	4,400	1,100	290	1,000	700	1,000
1 min maximum		58	5.9	1.4	7	3.5	0.25	2.9	1.5
0.38		5.1	2.5	0.69	19	12	0.47	4.3	2.6
Mass (g)/kg agent		0.27	0.16	0.33	0.14	0.08	0.02	0.19	0.07
Total mass (g)		18	4.6	20	6.2	2.6	0.74	8.7	2.8

* Acetylene.

* Based on molecular weight of undecane.

L = Long-angle path.

R = Regular-angle path.

FTIR DATA

Test #9

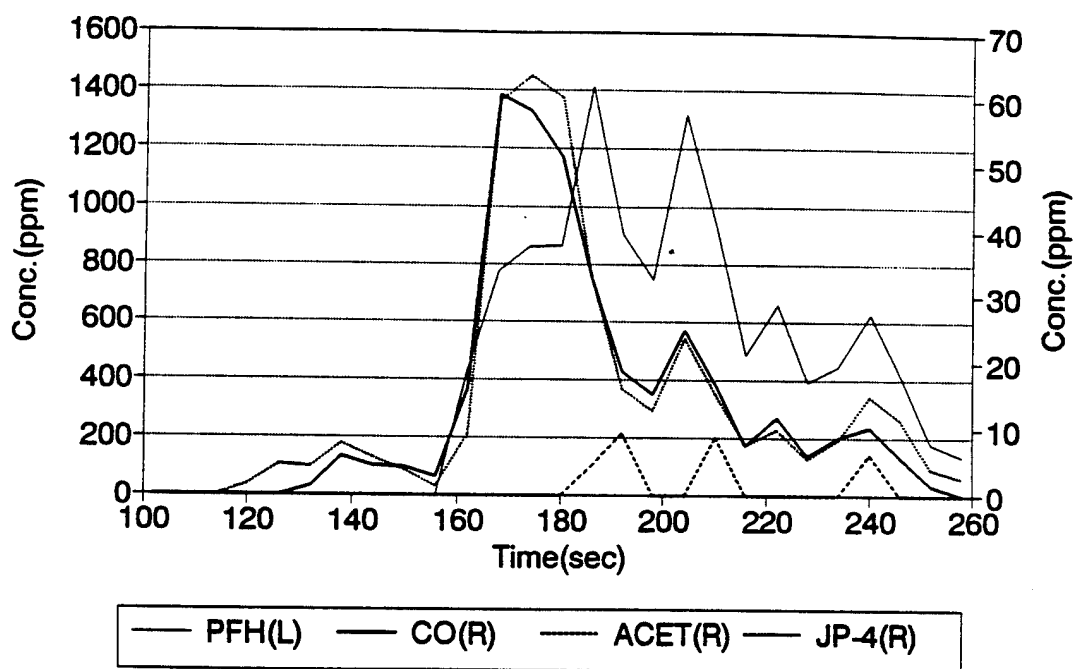
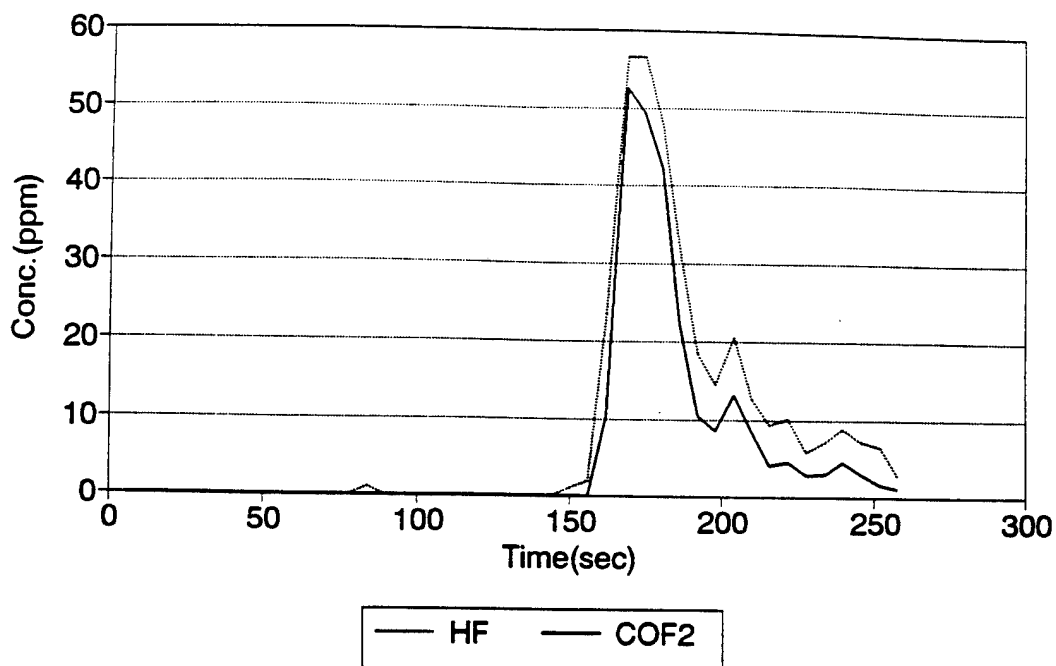


Figure 10. Example FTIR Concentration Plot.

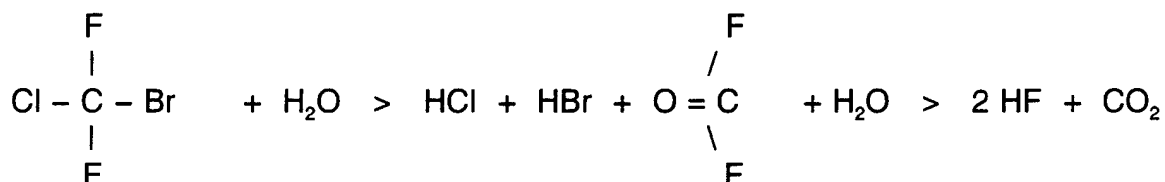
Since complete combustion of Halon 1211 (CClBrF_2) would produce HCl , HBr , and HF in the molar ratio of 1:1:2, these compounds were expected in the plume at the same ratio. However, the ratios measured during Runs 2 and 3 and the Screening Study did not reveal enough HF formation to bear out this expectation. The highest ratio seen was during Run 3, when the ratio approached 1:0.8 for HCl to HF . Thus, a significant part of the fluorine from Halon 1211 combustion was missing. If we add in the COF_2 observed, the ratios during agent application become 1:1.8:1.4 for Run 2 and 1:1.4:2.1 for Run 3. The COF_2 compounds decompose on contact with water to form two molecules of HF . If the HF concentration is considered equivalent to twice the COF_2 concentration, then the measured halogen acid ratios become reasonably close to the expected values, indicating that no other major fluorinated combustion products exist.

For HCFC 123 ($\text{C}_2\text{HCl}_2\text{F}_3$), the expected ratio of HCl to HF is 1:1.5, and after adding in the COF_2 contribution, the ratios become 1:0.9-1.2, still slightly on the low side. Thus, another fluorinated combustion product may still be present for HCFC 123. Another possible carbonyl compound is CF_3COCl , trifluoroacetyl chloride, which does not have a published spectrum.

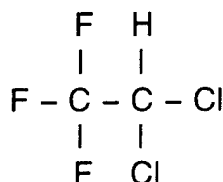
PFH has only fluorine present in the molecule, so no check ratio is possible. Perfluorobutylene (never detected) was on the original target compound list, but only PFH could reasonably produce such an unstable molecule during combustion. The other two agents would have to combine two to four molecules together to obtain a four-carbon compound.

Although HBr generation is not possible from either replacement compound, and HCl generation is not possible from PFH, the fluorine content and thus both HF and COF_2 production are higher with the replacement agents than with Halon 1211. A glance at the structures of all three agents below illustrates the situation. The C-F bond is much stronger than either a C-Br or a C-Cl bond. Therefore, Halon 1211 could be expected to split off both the Br and the Cl to form COF_2 rather than COCIBr , COFCl , or COFBr . This is an exact parallel to the formation of phosgene, COCl_2 , from carbon tetrachloride. HCFC 123 also has a CF_2 group to form COF_2 , and PFH has six CF_2 groups in its molecule. Therefore, COF_2 is a highly probable product for all three compounds. The only uncertainty is whether sufficient water vapor is present to complete the conversion to HF immediately.

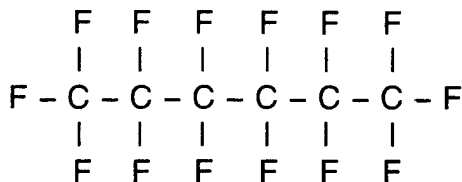
Halon 1211



HCFC 123



PFH



The FTIR successfully provided time-resolved plume data during the brief period of the exercises, identified an unexpected compound, carbonyl fluoride (COF_2), and provided detailed information on the most toxic gases present. The presence of the hot, visibly opaque, and turbulent plume did not seriously impair its performance. While it does not have enough sensitivity to detect trace components on small plumes, it can quickly screen for the typical immediate high-risk concentrations.

Because COF_2 was the most toxic compound found, and because its presence was unexpected, further explanation of the compound identification technique is necessary. The reference spectrum shows two bands that were the most useful for quantitation and identification, a sharp band at 774 wavenumbers and a broad doublet at 1900 to 1950. These two regions are shown in Figures 11 and 12. Each spectrum has been magnified to show the COF_2 band at maximum expansion. Absolute absorbances are not obtainable from these figures since the scale factor is different for each spectrum.

The 774 wavenumber band is obscured completely by HCFC 123 bands, but the region is clear for the other agents. The field spectra show slight band broadening due to nonlinear absorbance, but an exact match is seen with the reference spectrum. The 1900 to 1950 wavenumbers band has a few water bands superimposed in the field spectra but, again, the basic band shapes are identical to the reference spectrum.

Concentrations of JP-4 on Tables 19 and 20 are based on the molecular weight of undecane, which was the nearest average molecular weight for JP-4.

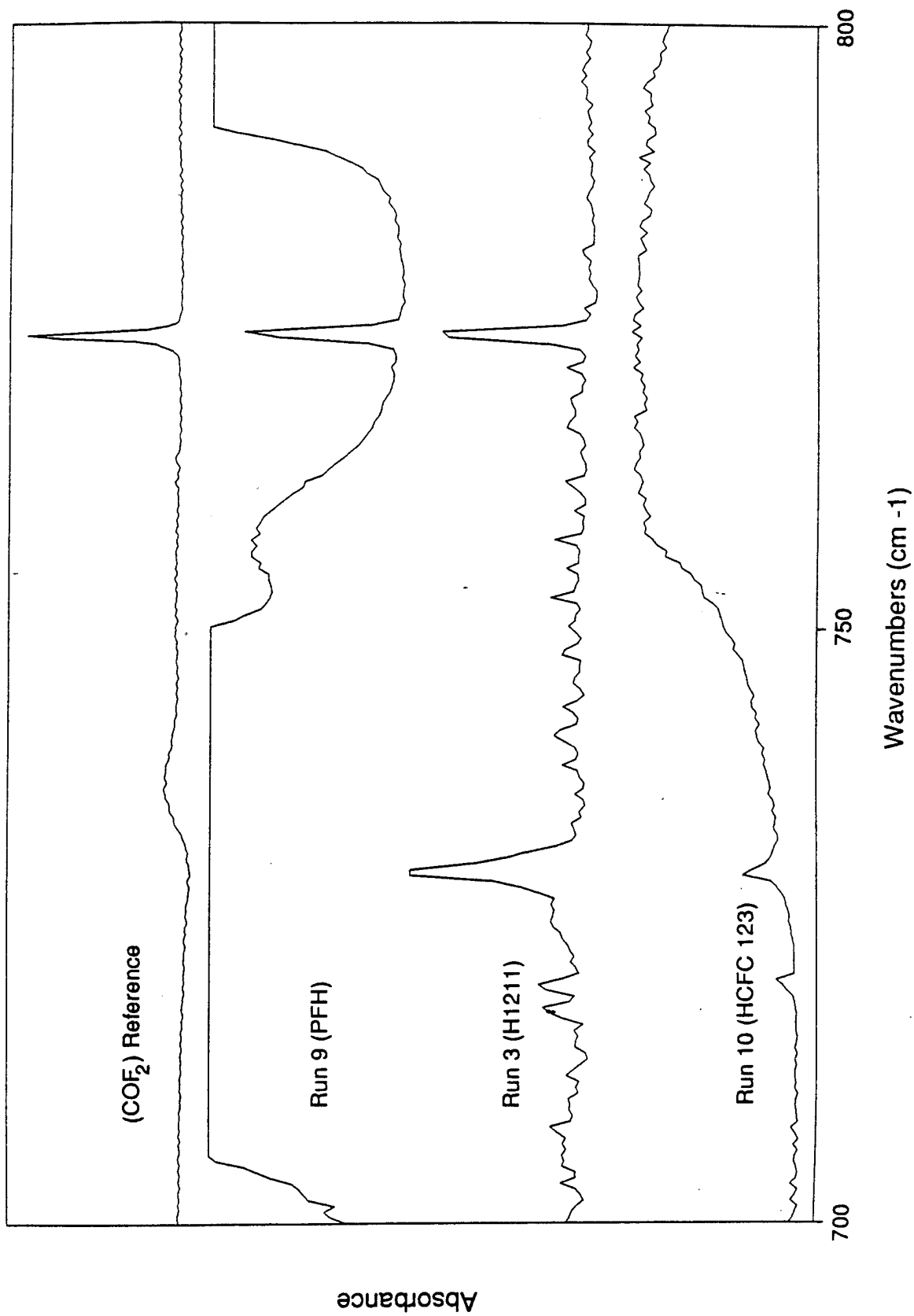


Figure 11. Comparison of carbonyl fluoride reference and field spectra at 774 cm⁻¹.

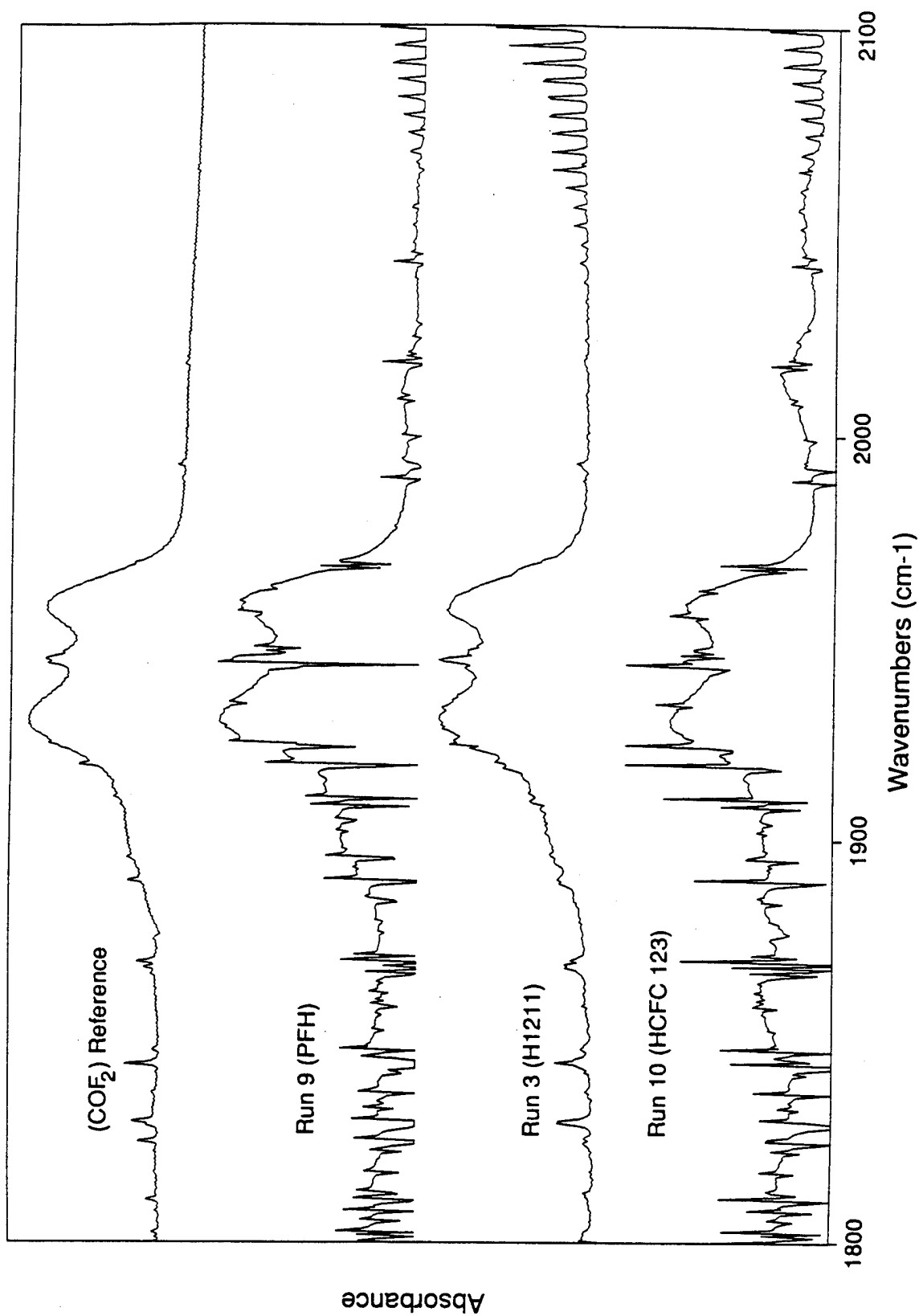


Figure 12. Comparison of carbonyl fluoride reference and field spectra at 1900 to 1950 cm⁻¹.

5. Vertical Profile Results

Table 21 shows the results of the GC analysis of the vertical profile samples for halocarbons. During Run 2, the samplers were too far away from the firefighter position to register a proper sample. Starting with Run 3, the samplers were moved next to the PUF sampler. The vertical profile shows higher readings near ground level, as was seen in the Screening Test, but a weaker gradient was observed due to the greater vertical dispersion when fighting a three-dimensional rather than a pool fire. This gradient shows that the normal firefighting practice of dropping flat to find breathable air would not be appropriate when halocarbon agents are in use.

TABLE 21. VERTICAL PROFILE EXTINGUISHING AGENT CONCENTRATIONS (ppm).

Height (in.)	Run 1 (no agent)	Run 2 (1211)	Run 4 (123)	Run 5 (123)	Run 6 (PFH)	Run 7 (PFH)
56	Blank	9.82	165.57	725.07	456.10	449.21
30		6.17	235.47	1407.62	388.79	614.05
8		4.98	938.04	4444.81	439.20	1696.75

6. Acid Gas Tubes Exposure Profile Results

Figures 13 through 15 illustrate Draeger tube placement and concentrations of the acid gases. The stain lengths were converted to equivalent individual gases using laboratory measurements of volatile response, and the gas ratios were measured by FTIR. Note that the upper concentration boundary is not known for both Halon 1211 and HCFC 123 since some of the stain tubes read offscale. No tubes were deployed during Run 3, and no tubes showed any readings (zero stain) for Runs 1, 4, 6, and 7. Table 22 shows the parts per million range of acid gases detected by the Draeger tubes. Calculations for this table are described in Appendix B.

TABLE 22. DRAEGER TUBE ANALYSIS FOR ACID GASES (ppm).

Acid gas	IDLH (ppm % _v)	Halon 1211 ^a	Halon 123 ^a	Perfluorohexane
		ppm	ppm	ppm
HF	30	1.8 - 30	4.1 - 260	16 - 119
HCl	100	3.2 - 54	8.3 - 410	—
HBr	50	5.7 - 98	—	—
COF ₂	15 ^b	1.4 - 24	2.5 - 120	13 - 91

^a Upper range values are minimums, tubes read offscale.

^b Estimate from equivalent HF formation.

Test # 2 - Halon 1211

Oct. 15, 1991

12:30 pm

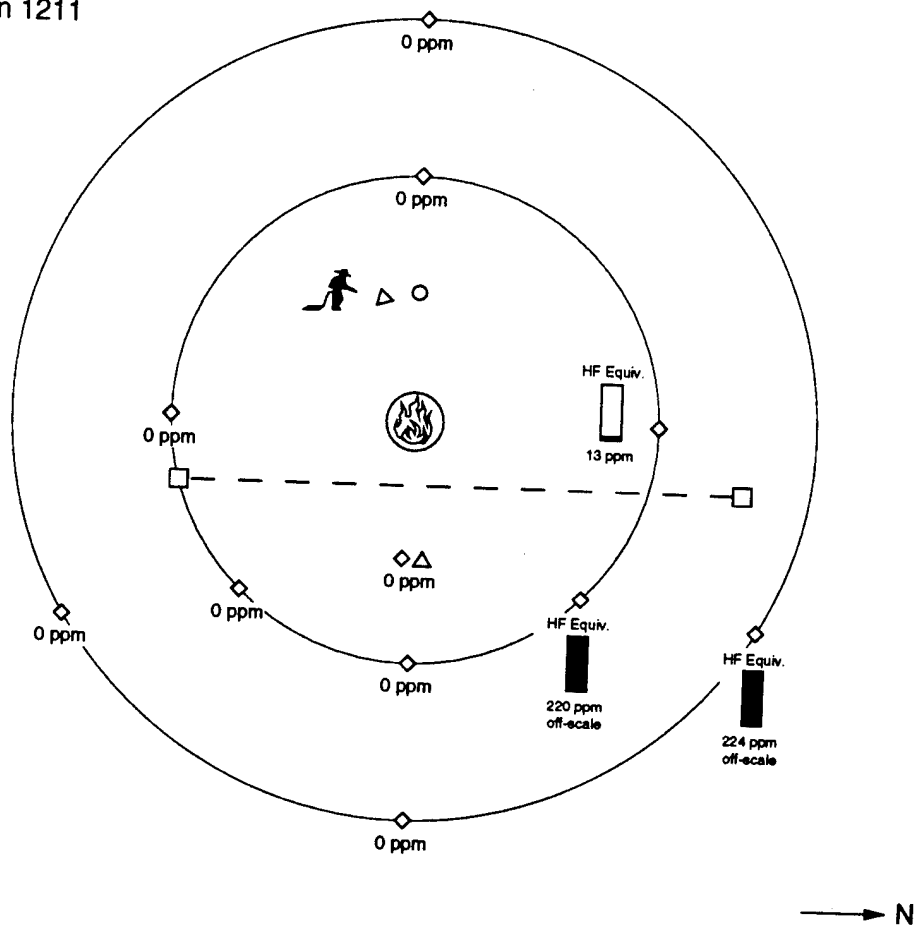


Figure 13. Run 2—Halon 1211.

8:40 am

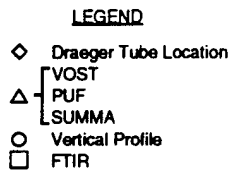


Figure 14a. Run 5—HCFC 123.

12:05 pm

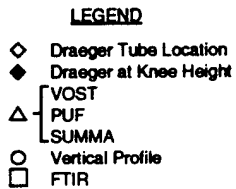


Figure 14b. Run 10—HCFC 123.

Test # 8 - Perfluorohexane

Oct. 18, 1991

11:15 am

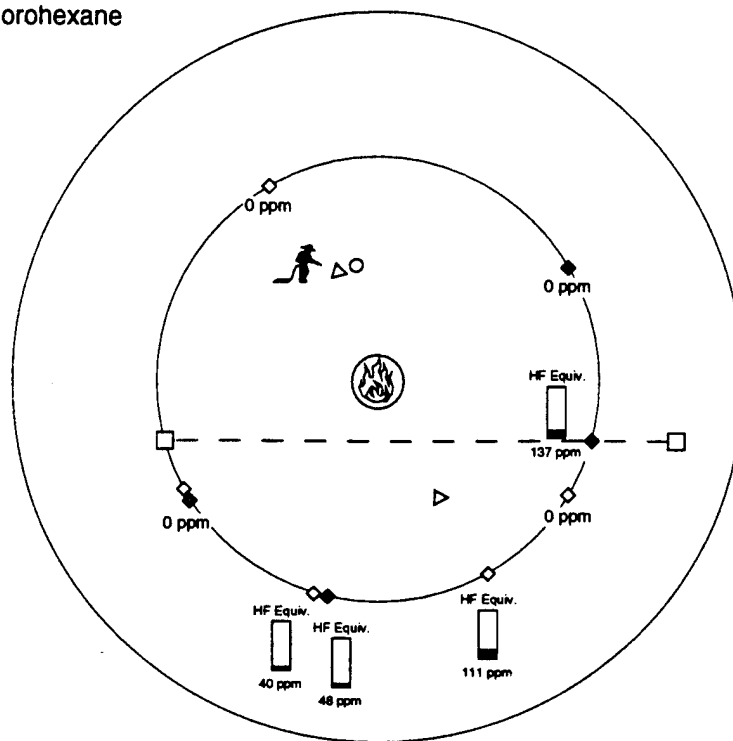


Figure 15a. Run 8—PFH.

Test # 9 - Perfluorohexane

Oct. 18, 1991

11:45 am

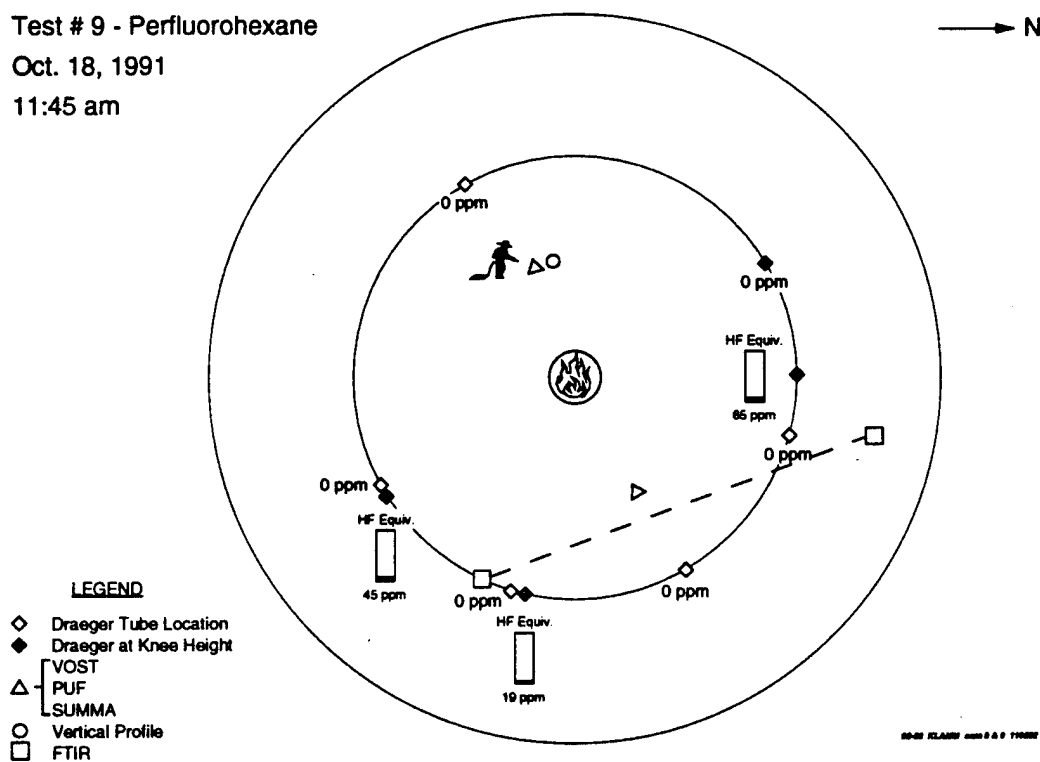


Figure 15b. Run 9—PFH.

C. SAMPLING PROCEDURES

The following sections describe the sampling equipment and procedures used for the Main Test. Procedures covered include Summa[®] canisters, Tenax[®]/charcoal samplers, PUF samplers, FTIR, vertical profiles, and acid gas tubes.

Note that all plume samples were collected from a common probe located within the plume. The probe was built using 5/8-inch inside diameter Teflon[®] tubing to reach about 25 feet into the air. A protective sheath of stainless steel tubing wrapped with ceramic fiber insulation protected the Teflon[®] tubing from heat.

The lower end of the plume-sampling probe was connected to the plume-sampling manifold. This manifold provided sample splits to the PUF, Summa[®], and Tenax[®]/charcoal samplers. The PUF sampler pump provided the suction for drawing sample through the manifold, and the tap lines for the Summa[®] and Tenax[®]/charcoal branched off. The manifold itself was made from a section of stainless steel pipe fitted with 1/4-inch Swagelok connectors for attaching the various sample tubes. The manifold fit directly onto the PUF sample intake, just upstream of the PUF particulate filter.

1. Summa[®] Passivated Canisters

Summa[®] passivated canisters were set up to sample the plume, firefighter, and downwind locations. One upwind (background) sample was also collected. Plume samples were collected using the plume-sampling manifold, while firefighter and downwind location samples were drawn directly into the appropriate canister. Canisters were set up on stands to provide a sample intake height of about 1.4 meters at all locations. The initial canister vacuum was recorded before sampling.

Sample collection involved opening the main valve fully to allow sample to be drawn through the glass capillary at critical velocity. Sample collection then proceeded for a total of roughly 6 to 8 minutes—concurrent with the other sampling methods. Thus sampling continued for several minutes after the fire was out to allow adequate collection of fumes, smoke, and so forth.

After the sample was collected, the Summa[®] canisters were sealed by closing the main valve and removing the glass capillary. The vacuum within the canister was measured and recorded on the field data sheet. Each canister was then attached to a dry nitrogen line and filled with dry nitrogen to 200 mm Hg. The pressurized canisters provided a stable environment for shipping samples back to the laboratory for analysis and identified invalid samples due to leaks. An identification tag was attached to each canister with the serial number, sample number, location, and date.

2. Tenax®/Charcoal Samplers

The Tenax®/charcoal sampler consisted of an adsorbent resin trap (cartridge), a sampling pump, a calibrated dry gas meter, and a rotameter. The cartridge contained approximately 1.0 gram of Tenax® and 1.0 gram of charcoal. Each cartridge was embossed with a unique sample number at one end of the glass tube. A known volume of air was collected from the plume manifold air stream and drawn through the cartridge at a known flow rate of approximately 1.0 L/min. Samples at the firefighter and downwind locations were drawn directly into the resin trap. The maximum air volume collected was 10 liters. The sample collection method was based on procedures described in USEPA's *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air*, Method TO2, with modifications. Except for the change in adsorbent packing, the sample preparation procedure used in the Screening Study was unchanged.

3. PUF Samplers

As with the other stationary methods, PUF samplers were set up to sample the plume, firefighter and downwind locations. One upwind (background) sample was also collected. Plume samples were collected using the plume sampling manifold, while the other samples were drawn directly into the appropriate sampler. Samplers were positioned on-site as determined to give the most representative samples.

PUF sample collection followed EPA Method TO4 with respect to installation of the PUF sample cartridges. Latex or cotton gloves were used to prevent contamination of the cartridge. After the cartridge was inserted, power was turned on and the run began. Sample was collected for the next 6 to 8 minutes.

The PUF particulate filters were weighed prior to being sent to the field, and then they were placed in individually marked petri dishes. Petri dishes were cleaned with distilled deionized water and methanol before use. No other procedure changes were made from the Screening Study.

4. FTIR

The FTIR source (Midac 50-cm diameter) and spectrometer (Midac 2400 with KBr optics and mercury-cadmium-telluride detector optimized for operation between 400 and 4500 cm^{-1}) were located just outside the inner windscreen on opposite sides of the fire pit. The line of sight was positioned such that the breathing zone just downwind (1 meter) of the fire pit was sampled. During three of the tests, the beam path was skewed slightly to measure the composition in a cooler portion of the plume (refer to Figure 4) to better represent typical downwind firefighter exposure. The following instrument settings were used:

- Single 0.5-second FTIR scans were collected every 6 seconds during the tests.
- Instrument resolution was set to 0.5 cm^{-1} .
- Total path length was 36 meters, although effective path length (that portion of the path within the plume) was estimated at 5 meters (7.4 meters for long-angle scans).

In all tests, sampling by the FTIR was continued for 2 to 3 minutes after agent application ceased to account for smoke and other off-gas formation.

5. Vertical Profiles

The evacuated stainless steel tanks (similar to Summa® canisters, but without special internal coatings) for agent measurements of the vertical profile were operated in a manner identical to the Summa® canisters. In each case, the initial canister vacuum was recorded before sampling. Prior to testing, three canisters were placed on a specially built stand designed to hold the canisters at ankle, waist, and breathing height. Glass capillary tubes used to draw sample at critical velocity were identical to those used with the Summa® canisters. Following each test, the stainless steel tanks were pressurized to 200 mm Hg with dry nitrogen for shipping stability. Data forms and the sample ID system were also identical to those used with the Summas®.

6. Acid Gas Tubes

Draeger length-of-stain sampling tubes for HF were positioned around the double-ring test site, primarily on the downwind side. The specific locations for each test are shown in Figures 21 to 23. Each tube was placed at breathing height, except for those indicated in Tests 8 to 10, which were at knee height.

The tubes were operated with Du Pont ALPHA-2 battery-driven pumps. The flow rate for each pump was set at 100 ml/min. The tubes contain Bromophenol blue, an acid/base indicator that reacts with acidic hydrogen to produce a color change from blue to yellow. Therefore, the presence of each acid gas (HF, HBr, HCl, COF_2) affects the length of stain. The range of response for Draeger tubes is between 0 and 37 μl HF.

Before each test, all pumps were calibrated against a bubblemeter with used Draeger tubes in place. The ends of a new tube were then broken off and inserted into the pump. At test completion, 500 cm^3 of clean air were passed through each tube to filter through any unreacted gas. The tube was removed, and the stain level recorded on a data sheet. After tube removal, another tube (used) was inserted for the measurement of final flow rate. The average of initial and final flow rates was used for calculation purposes.

D. ANALYSIS PROCEDURES

1. Summa® Canisters

The analysis of samples collected by the Summa® canisters for the Main Test was based on several methods, including EPA Methods TO14, 5040, and 8260. In brief, the Summa® canister contents were transferred to an adsorbent tube (VOST trap), and a surrogate and internal standard were added. The VOST trap was then thermally desorbed onto an "analytical" trap, which also consisted of an adsorbent material, and the VOCs were further concentrated. The "analytical" trap was thermally desorbed directly onto a GC/MS system for chromatographic separation and mass measurement.

Prior to sample analysis, the analytical system was calibrated for proper performance with various instrumental checks, including mass calibration, proper mass tuning, three-point calibration curve, and system blank. All of these checks were performed daily, except for the three-point calibration curve, which was initially run to determine the response of each target analyte covering a predetermined concentration range. The limited number of analytes chosen for the Main Test were based on the Screening Study results. This analytical procedure also allows for the identification of "unknown" compounds or TICs.

2. Tenax®/Charcoal Traps

Samples collected on Tenax®/charcoal trap adsorbents were analyzed by GC/MS procedures, which are based on EPA Methods T02, 5040, and 8260. Most of the analytical approaches, in fact, are identical to the Summa® method. The samples collected on Tenax®/charcoal traps were initially spiked with surrogates and internal standards. The contents of the Tenax®/charcoal trap were thermally desorbed onto an "analytical" trap also consisting of adsorbent material. The contents of the "analytical" trap were then thermally desorbed directly onto a GC/MS system for chromatographic separation, followed by mass measurement. This procedure also allowed for the identification of TICs.

3. Polyurethane Foam (PUF) Cartridges

Extractable organics, both SVOs and PCDDs/PCDFs, collected on PUF cartridges, particulate filters, and probe rinses, were measured by analytical methods based on EPA Methods TO4/8270 and 8290, respectively. Precleaned and pre-screened PUF cartridges were fortified with selected "field surrogates," PCDD/PCDFs only, prior to their use for sample collection. Upon returning to MRI laboratories, PUF extracts were combined with the appropriate particulate filter and probe rinse extracts, and then split for the selective cleanup required for separate analyses of SVOs and PCDD/PCDFs by GC/MS techniques. The procedure for SVOs analysis allows for the determination of TICs. Briefly, the method involves the Soxhlet extraction of organics

from PUF cartridges, particulate filters, and probe rinses, using an organic solvent. The extract is then concentrated to a final liquid extract. A portion of each sample extract is taken through additional cleanup procedures for the selective analysis of PCDD/PCDFs.

4. FTIR

Each interferogram was converted to arbitrary Y form using the FFT function in Spectra Calc. The usual IR absorption plot was then produced by ratioing each scan to a "clear air" data set collected either before or after each test series along the same baseline. A detailed manual search of the most intense scan during each test was conducted using the Hanst Quantitative Library, supplemented by reference scans of the firefighting agents and JP-4, recorded using a 22-m White cell. After eliminating features due to water and carbon dioxide, most of the IR spectra were clearly assignable to library spectra. About 1 percent of the spectra recorded were not useable due to scanning problems looking through the hot, turbulent plume. The resulting gaps were not serious enough to impair the data.

A sharp absorbance line at 774 cm^{-1} and a broad absorption between 1900 and 1960 cm^{-1} remained. A further search¹ revealed that a carbonyl fluoride absorbance line had been reported at 774 cm^{-1} . Examination of the original low resolution prism spectrum² indicated that the 1900 to 1960 band was also characteristic of carbonyl fluoride and that the other carbonyl fluoride bands were also present in the fire plume spectra. Reference spectra were then recorded at MRI for carbonyl fluoride in a 14-cm Teflon®-coated gas cell using two techniques—partial pressure dilutions with nitrogen in-cell or precision dilution in Tedlar® bags with immediate transfer to the gas cell. The two techniques agreed within 10 percent, and the more reproducible precision dilution spectrum at 63 ppm-m was used as the COF_2 reference spectra.

Neither graphic subtraction (too time-consuming) or absorbance at a single, characteristic wavenumber for each compound (high probability of noise or interferences) was judged to be suitable for quantitation. Instead, all interference-free reference spectrum bands were analyzed, and the median of the usable results was used. A set of automated Spectra Calc subroutines were written to accomplish this quantitation for each compound. Spectra showing sharp absorbance bands (HF , HCl , HBr , CO , and the 774 cm^{-1} , COF_2 band) used the net peak area. Spectra showing broad absorbance bands (JP-4 , halocarbons, and the $1900\text{-}1959\text{ cm}^{-1}$ COF_2) used net absorbance at selected points across each band. Because some of the compounds were found at concentrations far above the intensity of the reference spectra (see

¹ H.A. Szymanski and R. E. Erickson. *Infrared Band Handbook*, 2nd ed., Vol. 2, IFI/Plenum, New York, 1970, p. 772.

² A.H. Nielson, T.G. Burke, P.J.H. Woltz, et al. "The Infrared and Raman Spectra of F_2CO , FCICO , and Cl_2CO ," *J. Chem. Phys.*, 20(4): 596 (1952).

Halon 1211 band at 900 cm^{-1} in Figure 16), at least one very weak absorbance band was included in each data set. This generally required measurements of reference spectra at concentrations 10 to 100 times the library spectra.

Additional reference scans were conducted to verify the useable linear range for each compound. In general, broad absorbances are linear to at least 1.0 absorbance unit, and narrow absorbances are linear to about 0.1 absorbance unit.

5. Vertical Profiles

A Varian 2400 Gas Chromatograph (GC) equipped with a flame ionization detector (FID) was used to analyze all samples with the exception of Run 2. The column used was a J & W Scientific DB-1 Megabore (30 m, $5\text{ }\mu\text{m}$), which separates compounds primarily according to boiling point.

The Shimadzu GC-8A with electron capture detector (ECD) was used for Run 2 samples. The FID did not have the sensitivity required to detect the traces of Halon 1211 in these samples. A 1-meter glass column with Chromosorb 102 (90 to 100 mesh) was used. The ECD current was 1 nanoampere.

Samples were analyzed by direct injection. A Toshiba portable PC-based integrator was used for data acquisition. The integrator maintained computer-readable copies of the raw chromatograms.

The GC analysis conditions were:

	<u>Varian</u>	<u>Shimadzu</u>
Volume injected:	0.5 mL	0.25 μL
Carrier gas:	Helium	Nitrogen
Column flow rate:	19 mL/min	70 mL/min
Column temperature:	40°C ISO 20°C *	60°C
Injector temperature:	180°C 170°C *	200°C
Detector temperature:	210°C	200°C

- * In an attempt to increase retention time, dry ice was sprinkled on the column for Runs 1 and 5.

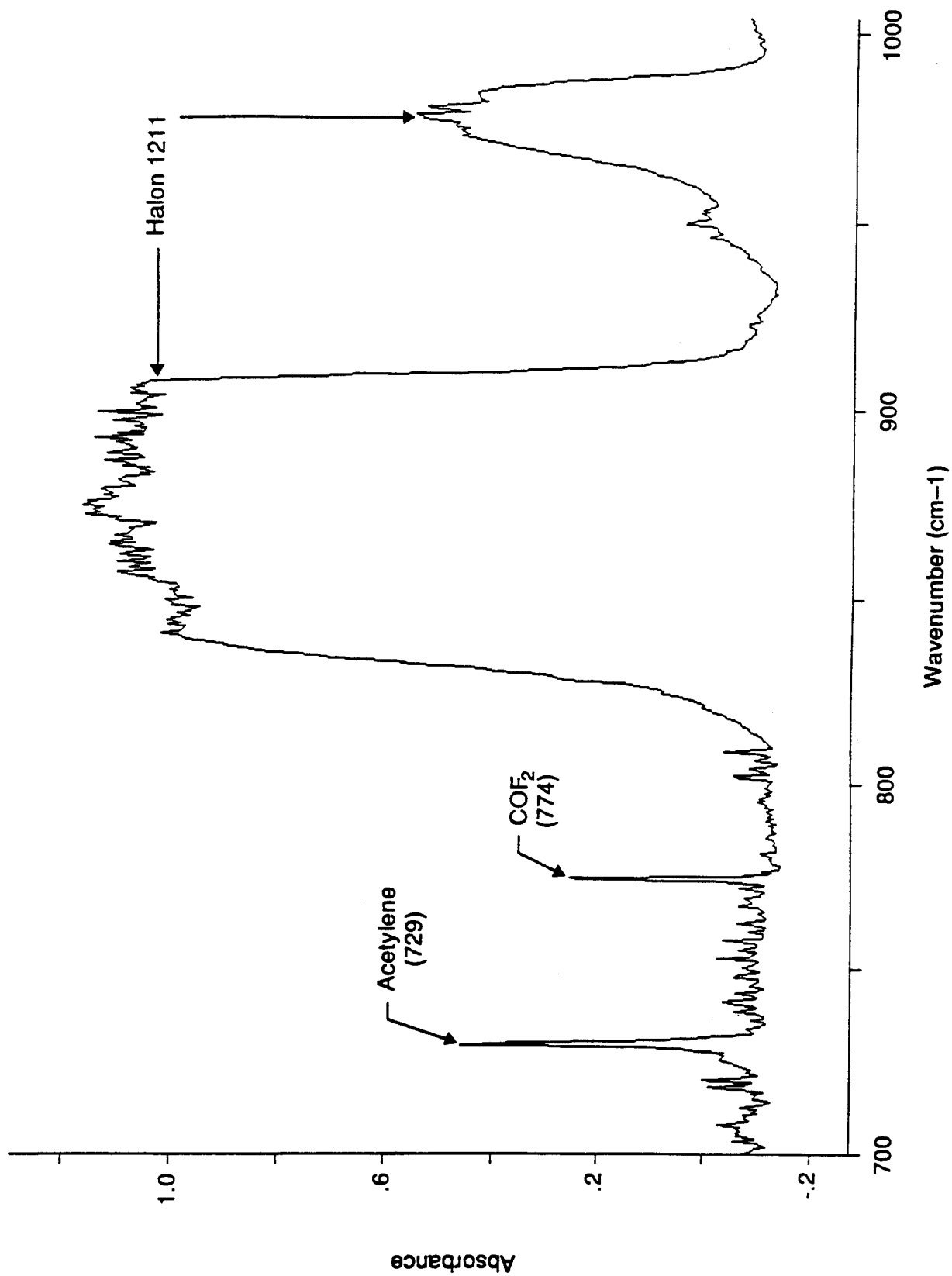


Figure 16. Portion of example spectrum.

Standard mixtures were prepared in Tedlar® bags. After filling the bag with a measured volume of prepurified nitrogen (using a calibrated mass flowmeter), a measured amount of each compound was injected into the bag with a syringe and mixed by flexing the bag. New standards were prepared each day of analysis.

Before starting each day's analysis, a standard of 100 ppm of the desired compound was analyzed (1 ppm for Run 2—Halon 1211). The standard was analyzed until the area results of two consecutive injections were within ± 10 percent of each other. The standard was again analyzed at the end of each day of analysis. The average of the daily initial and final standard response factors (RFs) for the 100 ppm (and 1 ppm) standard was used to calculate concentrations of the samples. In addition to the 100 ppm standard, a 150-ppm HCFC 123 standard was also prepared for Runs 3 and 4. The average daily RF for the 150-ppm standard was used in calculating the concentration of Sample 4016. Sample concentrations were calculated using integrated peak areas and were reported as ppm.

6. Acid Gas Tube Exposure Profiles

The acid/base indicator in Draeger tubes is sensitive to all acid gases, including COF_2 , which reacts with water immediately to form HF. Therefore, microliter HF readings from the tubes will not produce actual concentrations, but the HF equivalent. To determine the response factors, it was necessary to assess the response of each gas by itself when passed through a Draeger tube.

To accomplish this, samples of equal concentration were prepared for each gas in Tedlar® bags. The system for preparation was the same as for the precision dilution reference gases, FTIR, which was described in Subsection 5. A calibrated amount of sample was passed into each of three Draeger tubes. An average of the three readings was taken for calculation purposes. Response factors were determined relative to HF and were used in the determination of actual concentration.

E. SUMMARY

The Main Test, originally designed as a six-test series (one test of fire only, one test of Halon 1211, two tests each of HCFC 123 and PFH), was expanded to a ten-test series while in the field. The four additional tests included one repeat test due to equipment malfunction and three tests using FTIR long-angle path with Draeger tubes to better assess the acid-gas formations.

VOC results, obtained from the Summa® canisters and Tenax®/charcoal traps, showed significant levels of benzene, toluene, and halocarbons, but none exceeded the IDLH levels. The greatest concentrations were detected in the plume and downwind samples, with the lowest levels being found in the firefighter's breathing zone.

Semivolatile compounds and dioxin/furan results were obtained from the PUF samples, and showed significant, but less than IDLH, levels of JP-4, insignificant levels of some PAHs, and dioxins/furans near or below their detection limit. As with the VOCs, the greatest concentrations were detected in the plume and downwind samples, with the lowest levels being found in the firefighter's breathing zone.

Acid gas concentrations were measured by FTIR beam across the downwind edge of fire and by an array of Draeger tubes around the two circles of windscreens. These methods detected concentrations at or above IDLH levels for HBr, HCl, and HF, depending on the agent being tested. An unknown compound was also detected by FTIR, later identified as COF_2 , also near or above extrapolated IDLH levels. The acid gases showed the highest concentrations immediately downwind from the fire, decreasing gradually at greater distances within the plume boundaries.

The vertical profile samples showed the greatest concentrations of halocarbons near the ground, with the lowest concentrations at the firefighter's breathing height. This gradient shows that the normal firefighting practice of dropping flat to find breathable air would not be appropriate when halocarbon agents are in use.

SECTION IV

FIREFIGHTER EXPOSURE

This section discusses various aspects of risks to firefighters: acute hazards from gases; the transport modeling approach and results from the modeling process; the firefighter exposure using the actual site meteorology; the firefighter exposure using two worst-case assumptions for meteorology; and the degree of uncertainty in the results.

Appendix B, Subsection G, contains all exposure calculations (with example calculations) discussed in this section. Refer to that part of the appendix for further information regarding concentrations or emission rates.

Table 23 summarizes the published exposure limits for the various compounds found in the air samples. Due to the existence of published exposure limits, those compounds listed on Table 23 are either acutely hazardous or suspect carcinogen materials and will be evaluated for firefighter exposure risks if the exposure limits are exceeded. HCN and phosgene are included for comparison as well-known toxic compounds. The immediately dangerous to life or health (IDLH) value is the most appropriate limit because firefighter training and actual fire exposure are for only a few minutes of exposure. The LC_{50} limit leaves an inadequate safety margin in the event of overexposure, and the ceiling limits are intended for monitoring daily contact to toxic vapors.

The duration of extinguisher use is too short to apply the long-term (8-hour or more) limits, although the common PELs are included in the discussions which follow.

The following compounds exceeded one of the listed exposure limits (if a value was found), but were not evaluated for potential exposure for the following reasons:

- Benzene levels would exceed the proposed TWA of 0.1 ppm, but not the existing TWA levels. No IDLH values exist for benzene.
- Carbon monoxide was above the PEL concentration, but was well below the IDLH value.
- For Halon 1211, no exposure values were found to compare against.
- For HCFC 123, the MSDS recommended 1-minute maximum exposure concentration was exceeded.
- For JP-4, no STEL values were found; however, the NIOSH TWA of approximately 20 ppm was exceeded. In the absence of available STEL values, a comparison of observed JP-4 levels with the STEL for gasoline was made. The observed JP-4 levels were far below those for gasoline.

TABLE 23. EXPOSURE LIMIT VALUES IN PPM
(v/v, except where noted).

	PEL*	OSHA STEL	IDLH	NIOSH TWA
Benzene	10 ^a	5		1 ^c
Carbon monoxide	50	200 ^c	1500	35
Carbonyl fluoride	2	5	15 ^d	
Hydrogen bromide	3 ^c		50	
Hydrogen chloride	5 ^c		100	
Hydrogen fluoride	3 ^c		30	
Halon 1211				
HCFC 123	10 ^b	2500 (1 min) ^b		
JP-4 (kerosene)				100 mg/m ³
Particulate matter (carbon black)	3.5			3.5
PFH				
Toluene	100	150	2000	
Phosgene	0.1		2	
Hydrogen cyanide	10		50	

^a Proposed TLV for benzene is 0.1 ppm.

^b Recommendations from MSDS.

^c Ceiling values.

^d By extrapolation from HF.

* PEL is an 8-hour time-weighted average unless otherwise noted.

- For particulate matter, the smoke plume was essentially carbon black, which has a PEL of 3.5. This value was exceeded only in the plume location, where no direct firefighter exposure would be expected.
- For PFH, no exposure limit could be found to compare against.
- For toluene, none of the limit values were exceeded.

Carbonyl fluoride and the acid gases are discussed in the following subsection.

A. ACUTE HAZARDS OF ACID GASES

The term, acid gas, is used to collectively define HF, HCl, HBr, and COF₂. Table 24 lists the FTIR data tabulated in terms of the multiple by which the IDLH is exceeded. The data are presented in terms of the total acid gas exposure entries, because the four acid gases (HCl, HBr, HF, and COF₂) attack the human body by essentially the same mechanisms. The available toxicity data for carbonyl fluoride are also very limited. The assumption that its toxicity is due only to the production of two molecules of HF on contact with water may eventually be shown to be too liberal. The COF₂ molecule is structurally identical to phosgene (COCl₂) with fluorines substituted for the chlorine atoms in phosgene. In all cases, the total acid gas IDLH ratio is greater than one, and in most cases the individual acid gases also exceed their respective IDLH values.

TABLE 24. TOTAL ACID GAS PLUME CONCENTRATIONS (BY FTIR)
(units of IDLH multiples).

Beam angle	Regular	Regular	Long	Regular	Regular	Regular	Regular	Long	Long
Extinguishing agent	None	1211	1211	123	123	PFH	PFH	PFH	123
Test No.	1	2	3	4	5	7	8	9	10
During agent application	0	7.4	3.2	4.9	11.2	8.0	10.3	3.8	5.6
Worst case	0	3.6	2.5	1.4	17	17	10	4.1	5.3
1-min maximum	0	6.8	3.7	4.9	6.7	5.0	5.5	2.4	3.0

In Run 2 of the Main Test (Table 24 above), changing from a pool fire to a three-dimensional fire caused the exposures to become even higher when compared with the Screening Test. Using the equivalent worst-case concentrations, the combined toxicity of the three then known acid gases (HCl, HBr, HF) was 1.8 times the IDLH for Run 4 and 1.9 for Run 5 of the Screening Test. Including carbonyl fluoride, the toxicities increased to 2.4 and 2.9 the IDLH, respectively. As shown by the time plots (Figures C-6 to C-14), concentrations of all compounds occasionally reached much higher peaks.

The elimination of HCl and/or HBr for the two replacement agents (HCFC 123 and PFH) is offset by the increases in HF and COF₂ formation. This is best seen in the agent application values, which are not affected by variations in extinguishment times. The average total acid gas concentrations at the close-in (regular angle) location are 7.4 times the IDLH for Halon 1211, 8.1 for HCFC 123 $[(4.9 + 11.2)/2]$, and 9.1 for PFH $[(8.0 + 10.3)/2]$. Long-angle average total concentrations, although using data for only a single run each, still exceeded the combined IDLH value by a greater degree when HCFC 123 and PFH were used (5.6 and 3.8 times the IDLH value, respectively) than when the Halon 1211 was used (3.2).

B. MODELING APPROACH

The Industrial Source Complex Short-Term (Version ISCST 90348) model is one of the family of air dispersion models maintained by the EPA. ISCST combines and enhances various dispersion algorithms into a computer program that can be used to assess the air quality impact of emissions from a variety of sources. This model was selected from an array of available dispersion models because it is an EPA-approved model, and it is a preferred model for short-term, simple terrain releases near ground modeling listed in the EPA document *Guideline on Air Quality Models (Revised)* (EPA, 1986) and Supplement A (EPA, 1987).

The ISCST model is designed to calculate concentration or deposition values for time periods of 1, 2, 3, 4, 6, 8, 12, and 24 hours. Virtually all dispersion models employ dispersion coefficients based on a nominal 10-minute arraying period. However, the same models apply those coefficients to 1-hour arraying periods to accommodate the most commonly available meteorological data. Thus, in our application which assumed that the test meteorological conditions as well as the emission rate persisted over an entire hour, the resulting 1-hour concentration should be representative of the concentrations during the firefighting period. Some of the major features of this model are:

- Choice of polar or cartesian coordinate system.
- Calculation of plume rise due to momentum and buoyancy as a function of downwind distance.
- Capability of simulating line, volume, and area sources.
- Variation of wind speed with height (wind profile exponent law).
- Consideration of time-dependent exponential decay of pollutants.

Because field observations recorded that the buoyant, billowing fire plume became essentially horizontal once agents were applied, it was necessary to ensure that ISCST could be used successfully to predict the proximate concentration field. This was done by running ISCST with the actual meteorology recorded during Runs 2 through 10 (see Table 7) and with the appropriate calculated emission rates, and then comparing the results with the respective Draeger tube measurements of acid gas concentrations.

A second modeling phase employed an EPA-developed set of "screening" meteorological conditions. This set of 49 wind speed/atmospheric stability classes (Table 25) was first developed for an early EPA dispersion model known as "PTMAX." These 49 combinations are also commonly used with the ISCST model to determine "worst-case" meteorology.

TABLE 25. FORTY-NINE-ELEMENT WINDSPEED/
STABILITY CLASS MATRIX.

Wind Speed (m/sec)	Stability Class					
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
0.5	X ^a	X		X		
0.8	X	X		X		
1.0	X	X		X		
1.5	X	X		X		
2.0	X	X	X	X	X	X
2.5	X	X	X	X	X	X
3.0	X	X	X	X	X	X
4.0		X	X	X	X	X
5.0		X	X	X	X	X
7.0			X	X		
10.0			X	X		
12.0			X	X		
15.0			X	X		
20.0				X		

^a "X" denotes combinations considered in modeling air quality impacts.

The following major assumptions, most of which are conservative, were made in each of the ISCST modeling runs:

- The terrain was considered flat.
- All receptor locations were at ground level.
- An arbitrary flow vector (180 degrees) was used to maximize the concentration in one direction during the actual meteorology run. During multihour simulations, the flow vector was randomly drawn from a uniform distribution over the range of 168.75 to 191.25 degrees.

- Ambient temperature for the runs was 293°K (70°F).
- The source emission rate was based on agent application period only.
- A unit emission rate of 1 g/s was used in each model run. The resulting concentration grid was multiplied by the target compound emission rate to produce the target compound concentration estimates.
- A source temperature of 294.26°K and an exit velocity of 0.01 m/s were used to reflect the nearly horizontal plume behavior observed during the tests. Results were compared against the Draeger tube measurements (see Subsection C below).

C. FIREFIGHTER EXPOSURE USING ACTUAL SITE METEOROLOGY

This subsection addresses firefighter exposure assessment based on the results of the dispersion modeling. To estimate the impacts of the field exercises, ISCST was applied using actual site meteorology and comparing the modeled results with the Draeger tube concentration measurements. The centerline concentration distribution obtained from modeling was used for conservatism. The calculation is shown in Appendix B.

1. Calculation of Exposure Factors

Formula 2 found in Appendix B, Subsection G, was used to estimate the acid gas emission rate by the ratio method. Several steps in this procedure add conservatism to the calculated emission rate. The highest 1-minute average detected agent and acid gas concentrations were used. Emission rates also were based on the measurable quantities of agent application. This treats all agents as being incorporated in the plume and compresses all acid gas emissions to only the agent application time.

Two methods for calculating emission rate were employed depending upon the agent being evaluated. The volumetric method for calculating emission rate compares sample volumes with the stoichiometric plume volume. This method must be used for dioxins and furans because no matching agent concentration is available for the applicable methods of detection. The volumetric method does not correct for the excess air present in the plume, and usually reports a plume volume about 10 times smaller than the ratio method. The second method employed was the ratio method. While the ratio method is not flawless, it is closer to the true situation in the plume.

2. Comparison of Draeger Results—Individual Acid Gases to ISCST Results

The information from the Draeger tubes was used to compare actual measurements of acid gas concentration to the ISCST results. Draeger tubes positioned on the inner and outer wind screens (as shown in Figures 13 through 15) provided acid gas concentrations at those locations. Each tube was located at breathing height, except for Runs 8, 9, and 10, which included Draeger tubes at knee height.

The raw range of response for the Draeger tubes was between 0 and 37 microliters of HF equivalent (or ppm with a 1-liter sample). The individual acid gas concentrations were obtained by correcting the total acid gas concentration (as HF) according to the relative stain response measured in the laboratory and assuming that the FTIR gas fractions correctly describe the mixture sampled by the Draeger tube.

For modeling purposes, discrete receptors were placed at the wind screen distances of 13 and 21.5 meters downwind from the center of the fire pit to represent Draeger tube locations and at other distances. The centerline concentrations obtained from modeling are shown in Table 26.

TABLE 26. MAXIMUM MODELED DOWNWIND CONCENTRATIONS.

Receptor Locations → m		5	10	13	15	21.5
Acid Gas Emissions	Emission Rates (g/s)	Short Term Concentrations for Albuquerque Field Test Operations (mg/m ³)				
HCl Run 2	2.32	549	436	314	257	146
HCl Run 3	0.74	175	139	100	82	46
HCl Run 4	6.21	1469	1168	841	688	390
HCl Run 5	8.94	2115	1681	1211	990	562
HCl Run 10	5.87	1389	1104	795	650	369
HF Run 2	0.7	166	132	95	78	44
HF Run 3	0.33	78	62	45	37	21
HF Run 4	1.71	405	322	232	189	107
HF Run 5	2.46	582	463	333	272	155
HF Run 7	1.56	369	293	211	173	98
HF Run 8	5.71	1351	1074	774	632	359
HF Run 9	3.77	892	709	511	418	237
HF Run 10	2.02	478	380	274	224	127
HBr Run 2	10.04	2375	1888	1360	1112	631
HBr Run 3	2.57	608	483	348	285	161
COF ₂ Run 2	1.84	435	346	249	204	116
COF ₂ Run 3	0.85	201	160	115	94	53
COF ₂ Run 4	2.44	577	459	331	270	153
COF ₂ Run 5	4.86	1150	914	658	538	305
COF ₂ Run 7	6.87	1625	1292	931	761	432
COF ₂ Run 8	14.93	3532	2807	2023	1653	938
COF ₂ Run 9	10.12	2394	1903	1371	1121	636
COF ₂ Run 10	3.19	755	600	432	353	200

The calculated Draeger tube concentrations were then compared to the modeled concentrations. Table 27 compares the highest acid gas concentrations measured by the Draeger tube during Run 2 to the maximum concentrations modeled using the average wind speed for Run 2.

TABLE 27. DRAEGER/MODEL COMPARISON—
RUN 2 (Halon 1211).*

	Draeger ^a (mg/m ³)	Model (mg/m ³)
HF	24.6	95
HCl	80.6	315
HBr	359	1360
COF ₂	64.7	249

* At distance of 13 meters.

^a The subject Draeger tube was saturated (offscale) at 224 ppm as HF. Actual concentrations could be significantly higher.

The modeled maximum concentrations, as expected, were higher than the saturated Draeger concentrations. Run 2, which was the Halon 1211 run with the highest detected agent and acid gas concentrations and highest stain level of the Draeger tubes, was chosen for comparison with the model. The logical consequence is that use of the ISCST model results should be considered as conservative.

Similarly, the highest HCFC 123 concentration was found in Run 5. The comparisons of the highest Draeger tube measurements and modeled maximums are shown below in Table 28.

TABLE 28. DRAEGER/MODEL COMPARISON—
RUN 5 (HCFC 123).^a

	Draeger ^a (mg/m ³)	Model (mg/m ³)
HF	103	185
HCl	375	515
COF ₂	204	349

^a Both measured at 13 meters.

Again, use of the model results appears to be conservative. The calculations for the tables above are shown in Appendix B.

3. Comparison to Draeger Results—Combined Toxicity

A comparison of ratios of cumulative acid gas concentrations to IDLH values is shown below. The individual acid gas IDLH values were combined to depict an overall acid gas IDLH, reflecting the fact that the acid gases present similar dangers to the human body. Table 29 below shows the measured Draeger tube IDLH exposure ratios as compared to the modeled IDLH exposure ratios at a 13-meter ring distance, with only the highest Draeger tube reading used for each run.

TABLE 29. CUMULATIVE IDLH EXPOSURE RATIOS
AT 13 METERS.

	Draeger (IDLH multiples)	Model (IDLH multiples)
Run No. 2	> 5 ^a	21
Run No. 5	> 18 ^a	38
Run No. 8	10	83
Run No. 9	5	56
Run No. 10	> 21 ^a	22

^a Tube readings were off-scale. Actual ratios could be much higher than the reported values.

Modeled exposure ratios are higher due to the conservative nature of the modeling projections in comparison to the Draeger tube readings. For example, the Draeger tube is not directly aligned with the center of the plume during an entire test. Nevertheless, this comparison indicates that ISCST results can be used successfully to assess exposures.

The IDLH exposure table (Table 30) uses the halocarbon runs with the highest agent and acid gas concentrations. These runs are respectively Run 2 for Halon 1211; Run 5 for HCFC 123; and Run 8 for PFH. Table 30 is based on modeled results using actual site meteorology. IDLH values are based on published levels of 30 ppm for HF, 100 ppm for HCl, and 50 ppm for HBr. The COF₂ value of 15 ppm is one half of the value of HF because COF₂ reacts with water to produce two molecules of HF.

TABLE 30. IDLH EXPOSURE TABLE—ACTUAL METEOROLOGY.

Distance (m) H1211 IDLH Exposure Multiples (Run 2)										
Compound	5	10	13	15	21.5	30	40	50	100	200
HCl	3.66	2.91	2.1	1.71	0.97	0.55	0.33	0.22	0.06	0.02
HF	6.9	5.48	3.95	3.23	1.83	1.04	0.63	0.42	0.12	0.03
HBr	14.4	11.44	8.24	6.74	3.82	2.17	1.31	0.88	0.25	0.07
COF ₂	10.88	8.65	6.23	5.09	2.89	1.64	0.99	0.67	0.19	0.05
Total	35.84	28.48	20.52	16.77	9.51	5.40	3.26	2.19	0.62	0.17

Distance (m) HCFC123 IDLH Exposure Multiples (Run 5)										
Compound	5	10	13	15	21.5	30	40	50	100	200
HCl	14.1	11.21	8.07	6.6	3.74	2.13	1.28	0.86	0.25	0.07
HF	24.25	19.27	13.89	11.35	6.44	3.66	2.21	1.49	0.43	0.12
COF ₂	28.75	22.85	16.46	13.46	7.63	4.34	2.62	1.76	0.51	0.14
Total	67.10	53.33	38.42	31.41	17.81	10.13	6.11	4.11	1.19	.33

Distance (m) PFH IDLH Exposure Multiples (Run 8)										
Compound	5	10	13	15	21.5	30	40	50	100	200
HF	56.29	44.74	32.23	26.35	14.95	8.5	5.13	3.45	0.99	0.28
COF ₂	88.31	70.19	50.57	41.33	23.45	13.33	8.05	5.41	1.55	0.44
Total	144.6	114.9	82.80	67.68	38.40	21.83	13.18	8.86	2.54	0.72

When using Halon 1211 to extinguish a fire, the four acid gases formed (HCl, HBr, HF, COF₂) present the greatest hazard. Results of modeling indicate that all four gases are near or above their respective IDLH limits at breathing height in the downwind plume, at distances of up to 30 meters from the fire. Conservative modeling calculations show that the combined toxicity of all four gases may still be hazardous up to 80 meters downwind.

When using the two replacement agents, HCFC 123 and PFH, the respective elimination of HBr and HCl offgases is offset by increases in HF and COF₂ concentrations. For HCFC 123, the modeled individual IDLH limits were exceeded up to 50 meters distance, while the combined IDLH was exceeded up to 100 meters. For PFH, modeled individual and combined IDLH values were exceeded at distances up to 100 and 180 meters, respectively. The PFH modeled results may have been perturbed by the modeling assumptions. Differences between the model and Draeger tube exposures indicate that the PFH exposure zones should be similar to the other two agents.

The "total" row for the acid gas effects represents a weighted sum of the individual IDLH exposure ratios at various distances from the source. The acid gases all attack the human body in the same manner; therefore, the summed effects are the levels considered for each individual agent. The PEL for each of the agents are typically a factor of 10 lower than the IDLH for each of the acid gases.

D. FIREFIGHTER EXPOSURE USING WORST-CASE METEOROLOGY

This subsection addresses firefighter exposure using 49 wind speed/stability class worst-case meteorology. ISCST may be applied in a "screening" mode to estimate potential short-term impacts from firefighter training exercises. In this approach, meteorological conditions were defined in terms of a 49-element wind speed/stability class matrix (Table 25). The matrix contains six stability classes that represent atmospheric conditions ranging from very unstable (Stability Class A) to very stable (Stability Class F). Each stability class is associated with a set of empirically determined dispersion coefficients. The wind speed elements of the matrix vary, depending upon stability class. The matrix is shown as Table 25.

The ISCST model was used to predict the nominal 1-hour concentration values for each of the 49 wind speed/stability class combinations at various downwind distances from the fire pit. These locations are defined as 5, 10, 13, 15, 21.5, 30, 40, 50, 100, and then 100-meter intervals from the source out to 1 kilometer.

As the next step in this modeling approach, the predicted values were examined to determine which of the 49 wind speed/stability class combinations produced the maximum predicted concentration for a given distance from the source. This "worst-case" was found to be the combination of a wind speed of 0.5 m/s and D-class

atmospheric stability. Next, the IDLH levels were calculated for the total acid gas impact, as shown in Appendix B. The results are shown in Table 31.

Figure 17 shows the IDLH and PEL exposure zones at any moment in time for the highest calculated emission rate. The IDLH level is exceeded to a distance of 260 meters. The PEL level, which is typically a factor of 10 lower than the IDLH, is exceeded out to 680 meters.

E. EFFECTS OF UNCERTAINTY

Many of the time-weighted methods of reporting results used in this report can lead to skewed results when comparing the different agents. The worst-case method of assuming that all emissions occurred only during the fire phase is usually conservative, since the FTIR time plots show varying degrees of lingering concentrations after extinguishment. This possible error is greater during tests when the fire was quickly extinguished. The integrated organic results err in the opposite direction because they had to be started a few minutes before ignition and could not be stopped until a few minutes after extinguishment. Thus most of the time they were sampling relatively clean ambient air, not combustion gases. Both of these methods can lead to concentrations in error by a factor of 10 or more.

Draeger results tend to be biased low because the plume was usually narrow and wandering. Thus none of the tests probably resulted in the center of the plume coinciding with any of the samplers.

If one studies the FTIR time plots carefully, the ratio of agent concentration to the acid gases tends to remain relatively constant regardless of the amount of agent applied, the extinguishment speed, or the beam location. Since this method of reporting results in the least scatter when different tests are compared, our risk calculations used primarily these ratios of agent to toxic gases. Then, the critical factor becomes the amount of agent used. Other scenarios using JP-4 fires should be directly scalable to our results if the amount of agent applied is known.

The test design did not include a sufficient number of tests at any particular test condition to develop any statistically based estimates of uncertainty.

F. SUMMARY

The four acid gases, HCl, HBr, HF, and COF_2 , at or above IDLH levels represent the greatest threat to the firefighter, and their impact is additive since they all attack the human body by essentially the same mechanisms. When the toxicities are combined in this fashion, the total toxicity ranged from 2 to 17 times the IDLH limit in the plume, depending on the exact test and extinguishing agent used. Averaged total toxicities were 7.4 times the IDLH for Halon 1211, 8.1 for HCFC 123, and 9.1 for PFH.

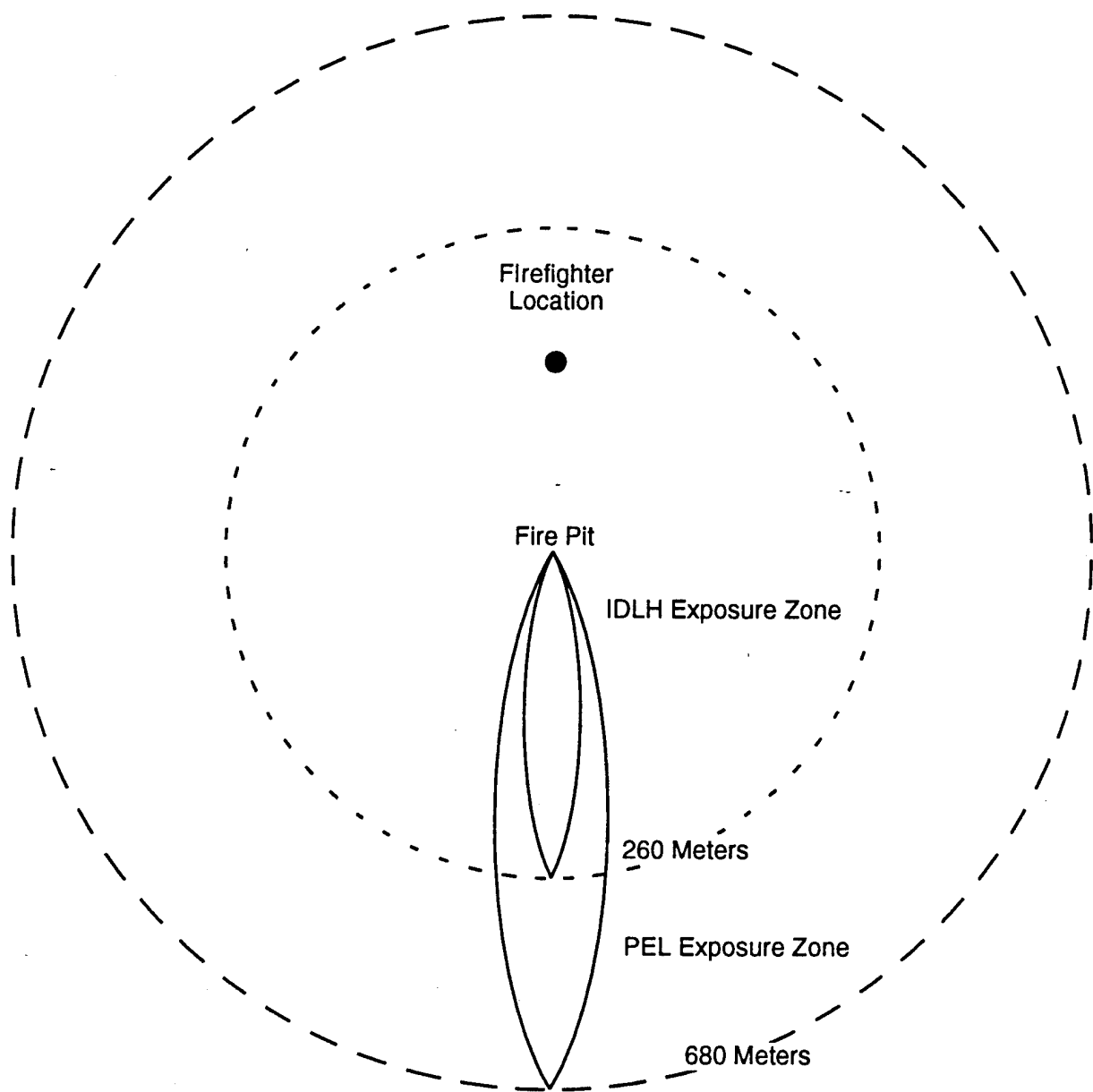
TABLE 31. IDLH EXPOSURE USING WORST-CASE METEOROLOGY.*

Distance (m) H1211 IDLH Exposure Multiples (Run 2)												
Compound	5	10	13	15	21.5	30	40	50	100	200		
HCl	26	8	5	4	2	1	1	0.4	0.2	0.1		
HF	50	15	9	7	4	2	1	1	0.3	0.1		
HBr	105	31	20	15	8	4	3	2	0.7	0.3		
COF ₂	80	24	15	12	6	3	2	1	0.5	0.2		
Total	261	78	49	38	20	10	7	4.4	1.7	0.7		

Distance (m) HCFC123 IDLH Exposure Multiples (Run 5)												
Compound	5	10	13	15	21.5	30	40	50	100	200	300	
HCl	103	31	19	15	8	4	3	2	0.7	0.3	0.1	
HF	178	53	33	26	14	7	4	3	1	0.5	0.1	
COF ₂	210	63	39	31	16	9	5	4	1	0.5	0.3	
Total	491	147	91	72	38	20	12	9	2.7	1.3	0.5	

Distance (m) PFH IDLH Exposure Multiples (Run 8)												
Compound	5	10	13	15	21.5	30	40	50	100	200	300	400
HF	412	123	77	60	31	17	10	7	3	1	.6	0.4
COF ₂	646	193	121	94	49	27	16	11	4	2	1	0.6
Total	1058	316	198	154	80	44	26	18	7	3	1.6	1.0

* Wind speed of 0.5 m/s and D-Class atmospheric stability.



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Figure 17. Firefighter exposure zones.

Downwind concentrations of the above compounds were modeled using the ISCST Version 90348 dispersion model from EPA. Worst-case meteorology was determined with a PTMAX 49-element windspeed/stability class matrix. All models were run under conservative assumptions and were compared to actual Draeger tube measurements. As expected, the modeled maximum concentrations exceeded the actual Draeger concentrations by roughly a factor of four. The conservative model was used to calculate IDLH exposure levels up to 200 meters from the source, with the combined toxicity remaining above IDLH levels beyond 100 meters from the source. Under worst-case modeling conditions, IDLH was exceeded up to 260 meters from the source, and the PEL was exceeded up to 680 meters.

SECTION V

COMMUNITY EXPOSURE

In this section, gaseous combustion products, which resulted from the firefighter training program, will be examined for human health impacts on the community residents. For exposure assessment purposes, a location was selected to represent the area of maximum exposure based on air dispersion model results and the impacts estimated for a resident at that location. The following sections describe the hypothetical exposure scenario to be used, the atmospheric dispersion models, and the results of the exposure assessment in terms of human health impacts.

A. EXPOSURE SCENARIO

The modeled exposure to the gaseous compounds produced during training exercises assumes an individual will be in an area of maximum concentration for a given period of time. For studies of a specific site, the residential area downwind of the training site is reviewed, and the actual residence located at the highest annual average ambient air concentration is selected. The individual at the nearest residence is defined as the maximum exposed individual (MEI). In this study, the experimental results obtained from tests conducted at one site will be used to predict the community exposure levels at any hypothetical site within the United States. Since the exposures assessed in this study are not specific to any site, modified procedures will be used to define maximum exposure.

The previous section showed that the impact parameters used in the Industrial Source Complex Short-Term (ISCST) dispersion model resulted in a maximum concentration very close to the source (within 100 meters). The assignment of a residence at that distance from any military installation training site did not appear to be realistic. Based on experience with other exposure assessment studies for chemical production emissions or incineration facilities, a distance of 500 meters to the nearest residence appears to be more realistic.

For the community exposure assessment, three exposure periods were selected: two short-term exposures and one long-term exposure. The two short-term exposures selected were for 15 minutes and 8 hours, corresponding to time periods for which regulatory exposure limits exist and applying to compounds with acute health hazards. The long-term exposure was the standard 70-year lifetime coupled with annual average air concentrations and applying to compounds with chronic health hazards that exceed regulatory exposure limits. For the lifetime exposure assessment, two scenarios were used: worst case and a more realistic case. In the worst-case scenario, the conservative assumption was for exposure for 24 hours per day, 4 days per week. For this study, deposition was not considered to be a major exposure pathway, and inhalation was the only exposure pathway assessed.

Deposition was not considered because (1) none of the realistic exposure scenarios gave risks within two orders of magnitude of the 1×10^{-6} trigger point, and (2) no reasonable deposition mechanism can provide enough further concentration to overcome this margin of safety.

A protocol describing the modeling and risk assessment procedures to be used in this study was submitted for review by EPA personnel involved with the implementation of the requirements of the Clean Air Act Amendments, Title 6, Section 12, and the Pollutant Assessment Branch of the Office of Air Quality Planning and Standards. The two groups reviewed the protocol independently, and both groups concluded that the methods described in the protocol represented accepted Agency procedures. During a review of the EPA risk assessment procedures, the EPA Science Advisory Board (SAB) indicated that the worst-case approach appears to be overly conservative and yields unreasonably high risk levels. In light of these comments, it appears that the risk assessment procedures used in this study are very conservative and likely will result in risk estimates that are overly protective to the population of the community.

The more realistic long-term exposure scenario considers exposure on the 4 days per week that training exercises would be held, and the exposure duration is for 30 minutes per training exercise period. During a training exercise, the extinguishing agent is normally used for a very short time before the fire is extinguished. This scenario allows for the dispersion of the constituents produced during the fire extinguishment process and for exposure to the maximum concentration of these gases by the MEI for 30 minutes.

Modeling was based on training with Halon 1211. However, current U.S. Air Force policy has removed the Halon 1211 agent from firefighting vehicles and stated that there will no longer be any firefighter training exercises using this agent in these vehicles. Actual releases of Halon 1211 or the replacement agent are anticipated for only a limited number (approximately 47/year throughout the entire Air Force) of actual flightline fires. If the model were changed to reflect current policy, projected emissions would be much lower.

B. ATMOSPHERIC DISPERSION MODELING

The Industrial Source Complex Short-Term (Version ISCST 90348) model was used to estimate concentration values for the short-term releases. The community exposure model repeated the worst-case meteorological condition (wind speed of 0.5 m/s and D-Class stability) found in the second phase of the firefighter exposure modeling for periods of 8 and 24 hours. A "randomized" flow vector was also used in this modeling phase within the constraints of one cardinal direction during the entire multihour period. The approach employed in this phase is analogous to that used by ISCST to avoid unrealistically high concentration estimates when on-site meteorological measurements record persistently calm periods with the same wind direction.

Results from the volumetric method of firefighter exposure modeling were used in scale modeling in this section.

The Industrial Source Complex Long-Term (ISCLT) model, version 6, was used to estimate atmospheric dispersion between the source at the training site and a ground-level receptor that corresponds to the potential MEI. That is, the MEI is assumed to be located where ground level ambient pollutant concentrations are highest at a distance of 500 meters, even if this location is not currently populated. This definition is consistent with other risk-based guidance recently proposed by EPA.

In the present application, the ISCLT model was operated, using regulatory default options as defined by EPA modeling guidance.³ All the training facilities were assumed to be located in areas of flat terrain. Because nonspecific sites at any location in the United States were used for this assessment, meteorological input to the ISCLT model was in the form of regional climatologies rather than any particular set of complex terrain scenarios. These data were developed as part of previous MRI work⁴ and have been successfully employed in other MRI risk-based modeling efforts.⁵ Figure 18 delineates the climatic regions. For each region, the dispersion climatology represents the average of appropriate data from between three to six weather stations. Albuquerque, the site of the field tests, lies in Region 2. Further details on the regional data can be found in Cowherd et al.²

The maximum ambient air concentration ($\mu\text{g}/\text{m}^3$), based on a unit emission rate (1 g/s) of the combustion products, was compiled for each of the seven regions. Concentrations were obtained in ten-degree directional coordinates. Receptor distances from the source were in 100-meter increments from 100 meters to 2,000 meters and in 250-meter increments from 2,000 meters to 10,000 meters from the source. For each region, the maximum ambient air concentration occurred in the north direction. Among the seven regions, the highest maximum air concentration at 500 meters occurred in Region 1 and the lowest maximum air concentration occurred in Region 7. Region 2 showed the third highest maximum air concentration, behind Region 1 and Region 6.

³ USEPA, 1986. Guidelines on Air Quality Models (revised), EPA-4501 2-78-027R. Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711.

⁴ C. Cowherd, G.E. Muleski, P.J. Englehart, and D.A. Gillette, "Rapid Assessment of Exposure to Particulate Emissions from Surface Contamination Sites." EPA/600-8-85/002, prepared for U.S. Environmental Protection Agency, Office of Health and Environmental Assessment, Washington, D.C., February 1985.

⁵ P. Englehart, 1990. "Special Management Standards for Municipal Waste Combustion (MWC) Ash," Final Report; prepared by Midwest Research Institute for EPA Municipal Solid Waste Program; EPA Contract No. 68-01-7287, WA 66.

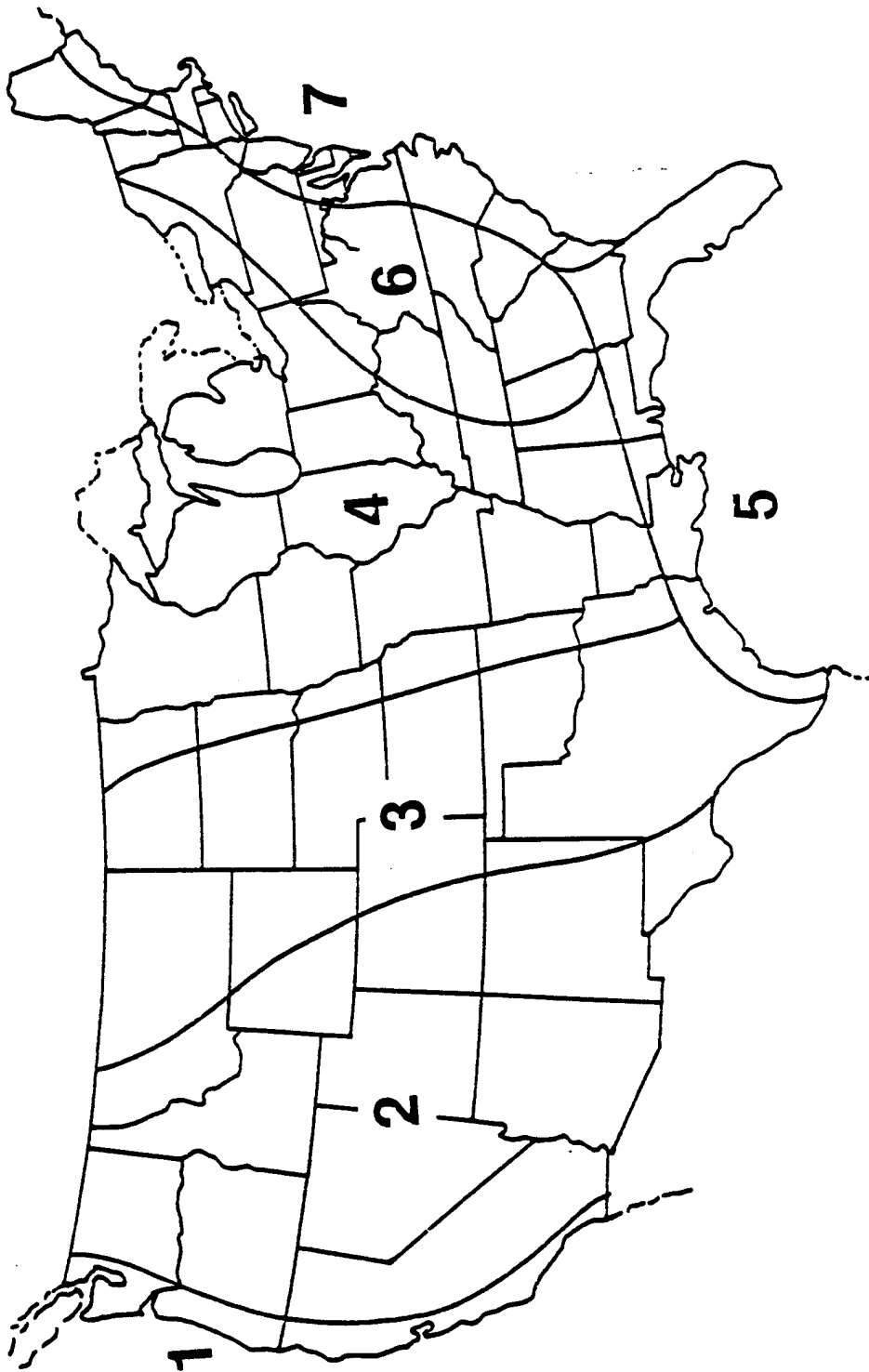


Figure 18. Climatic regions used for long-term dispersion modeling.

Figures 19, 20, and 21 show the model-predicted pattern of annual ambient air concentrations (isopleths) associated with emissions during the training exercises. Figure 19 is for Region 1, having the highest maximum air concentration; Figure 20 is for Region 7, having the lowest maximum concentration; and Figure 21 is for Region 2, the site of the field tests.

C. EXPOSURE ASSESSMENT

Use of the dispersion modeling discussed in the previous subsection requires emission rates in grams per second for each constituent. An approach using several conservative assumptions was used to calculate these emission rates. These assumptions were:

- Each training exercise would use 100 pounds of extinguishing agent and 20 gallons of JP-4.
- One training exercise was conducted per day and 4 days per week for 52 weeks per year for long-term exposure assessment.
- The emissions of constituents during each training exercise were spread over 15-minute durations.
- A 70-year lifetime exposure was assumed for Halon 1211 and HCFC 123; a 20-year lifetime exposure was assumed for PFH due to its expected product availability.
- Calculations for each constituent were based on the highest measured emission rate for the constituent during the period of extinguishing agent use.

In this approach, the emitted quantities of each constituent (e.g., HCl, HF, benzene), in pounds, were calculated by the FTIR ratio method for each extinguishing agent used in the field tests (i.e., Halon 1211, HCFC 123, and PFH). The calculated quantity of each constituent was grouped according to the extinguishing agent used in the test. Within each group, the weight of each constituent emitted was normalized to 100 pounds of extinguishing agent used. For each constituent in each extinguishing agent group, the maximum gas release, based on pounds per 100 pounds of agent, was selected. Since it was assumed that the total quantity was emitted over 15 minutes, the total quantity was converted to pounds per minute and then to grams per second. This emission rate was used for all dispersion model results, both short-term and long-term.

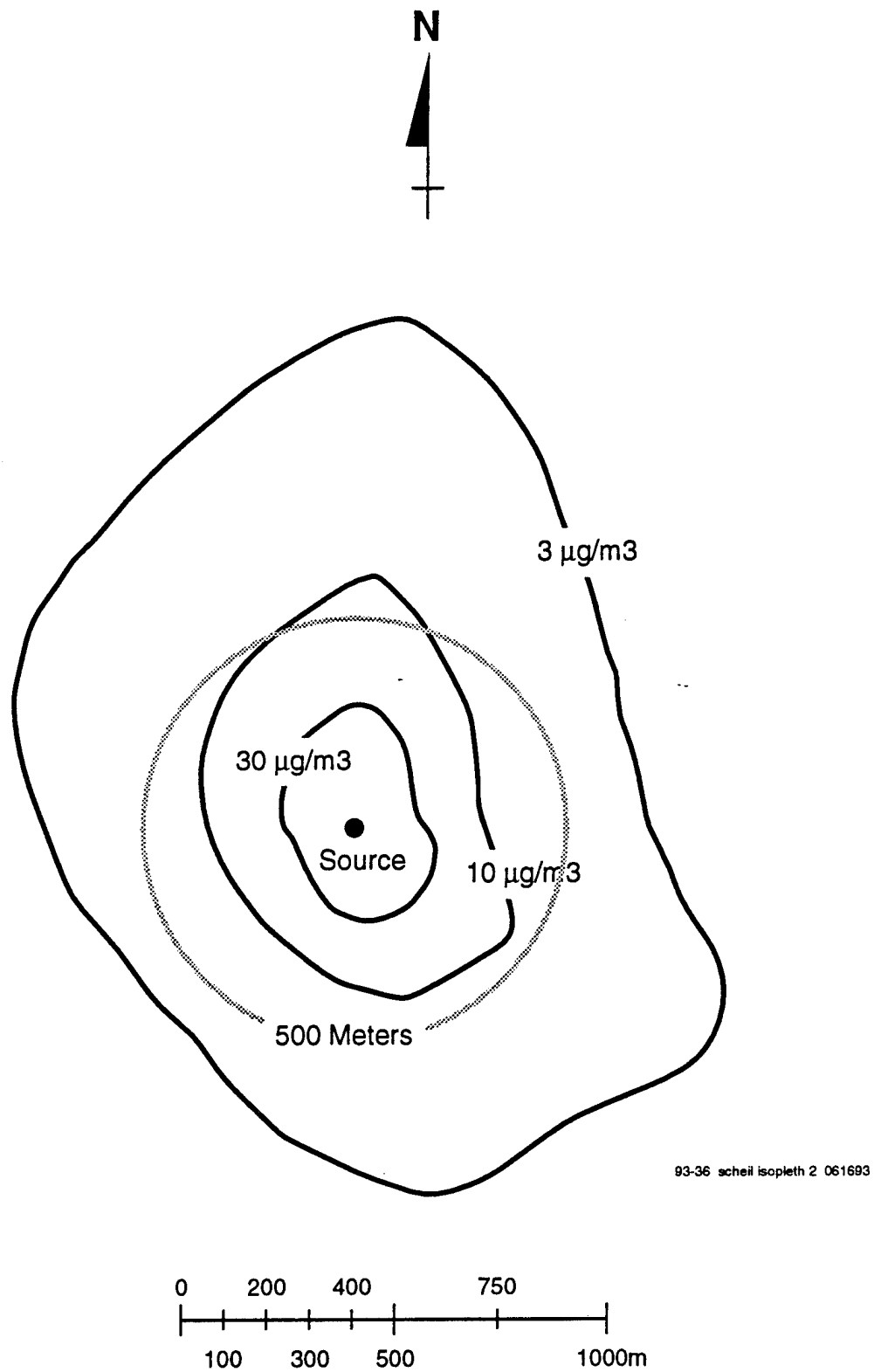


Figure 19. Normalized (i.e., unit emission rate of 1 g/s) isopleths for Climatic Region 1.

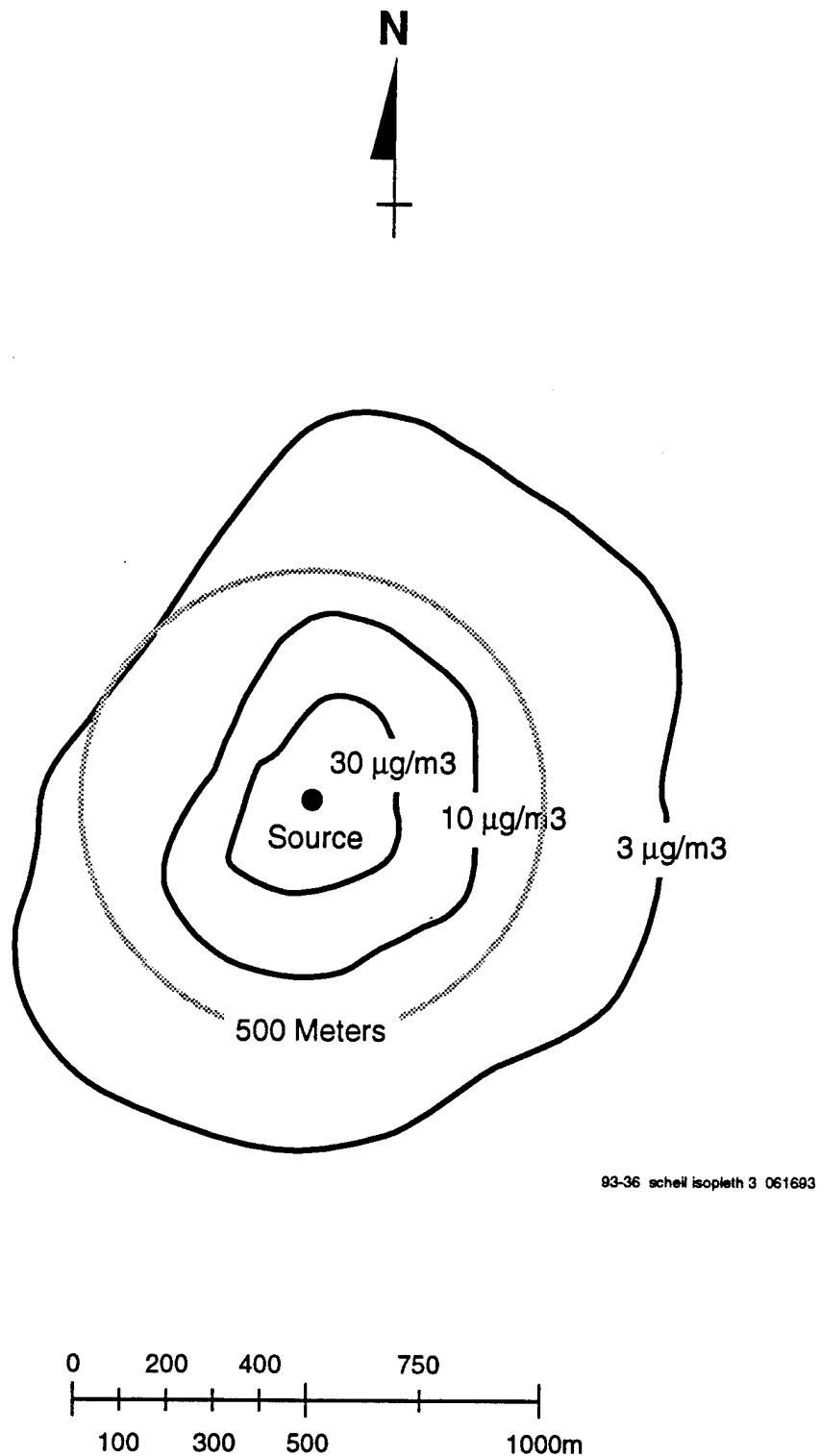


Figure 20. Normalized (i.e., unit emission rate of 1 g/s) isopleths for Climatic Region 7.

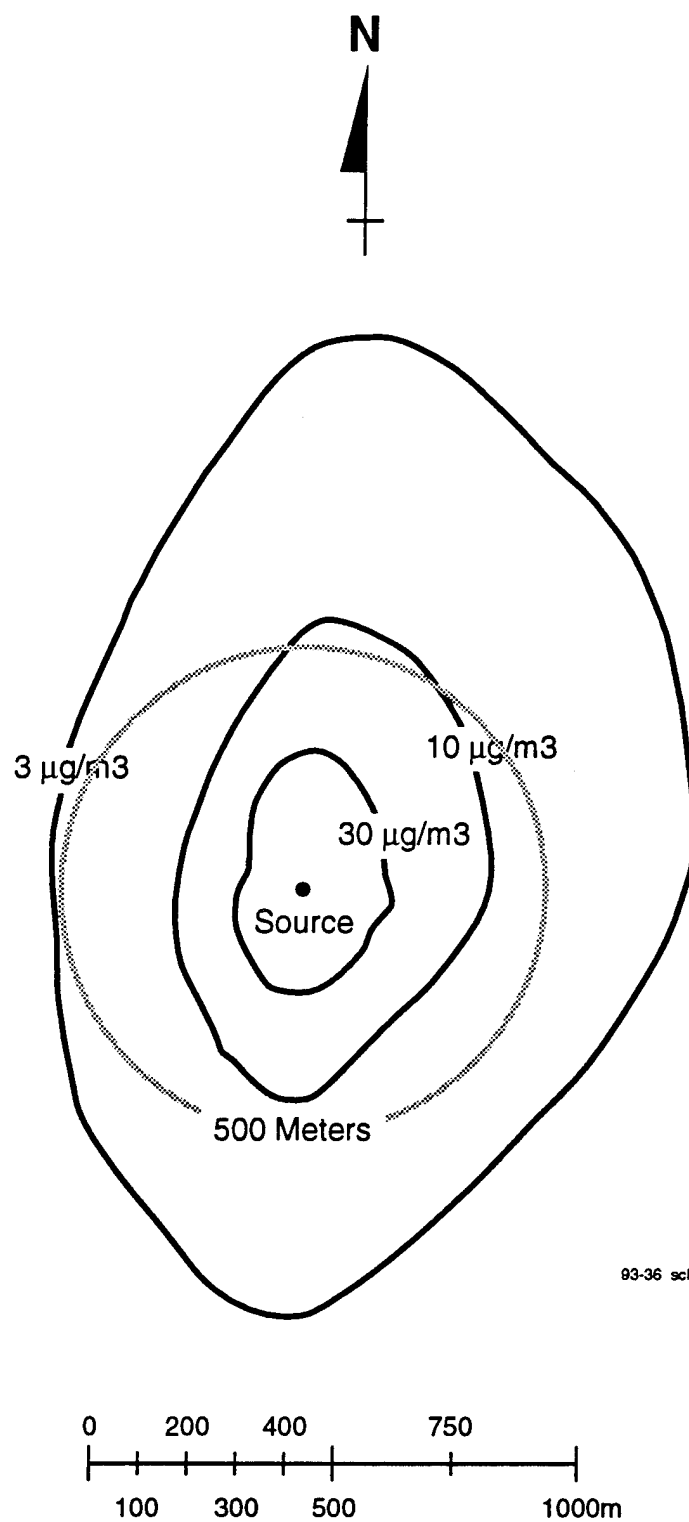


Figure 21. Normalized (i.e., unit emission rate 1 g/s) isopleths for Climatic Region 2.

1. Acid Gases

"Acid gases" is a term used to collectively define HF, HCl, HBr, and carbonyl fluoride (COF₂). The emission rates for each of these gases, based on the emission rate calculations described above, are listed in Table 32.

TABLE 32. ACID GAS EMISSION RATES FOR EACH HALOCARBON.

Agent	(g/s)			
	HF	HCl	HBr	COF ₂
Halon 1211	0.066	0.21	0.91	0.17
HCFC 123	0.33	1.2	NA	0.47
PFH	0.26	NA	NA	0.91

NA = not applicable

Using the results of the air dispersion modeling, the maximum ambient air concentration ($\mu\text{g}/\text{m}^3$) was calculated for each acid gas at a distance 500 meters from the source. For the long-term air concentrations, the emission rates were adjusted to compensate for the two exposure scenarios (worst-case and more realistic case). The results of these calculations are presented in Table 33. At the 500 meter distance, the levels for all the gases from all extinguishing agents are less than the 1991-1992 ACGIH permissible exposure levels (PEL) by at least two orders of magnitude and less than the IDLH levels from NIOSH by three orders of magnitude. See Table 23 for the respective PEL and IDLH values.

The EPA published a reference air concentration (RAC) for HCl emissions in conjunction with their 1991 Regulations for Boilers and Industrial Furnaces in the *Federal Register*. The RAC level for long-term exposure is $7 \mu\text{g}/\text{m}^3$. No RAC levels are available from EPA for the other acid gases. Comparison of the RAC level with the worst-case, long-term scenarios shows that the HCl levels from Halon 1211 are less than the corresponding RAC levels. For HCFC 123, the worst-case, long-term level exceeds the RAC in four of the seven regions. Using the more realistic long-term scenario, all HCl levels are less than the RAC.

TABLE 33. MAXIMUM AMBIENT AIR CONCENTRATIONS OF ACID GASES (500 METERS FROM SOURCE).

	Dispersion Model Scenario	Ambient Air Concentration ($\mu\text{g}/\text{m}^3$)									
		Halon 1211					HCFC 123				
		HF	HCl	HBr	COF ₂	HF	HCl	COF ₂	HF	COF ₂	PFH
Short Term	1. Maximum 15-min	5.0	15.8	68.5	12.8	24.8	90.4	35.4	19.6	68.5	
	2. Maximum 8-h	2.0	6.3	27.3	5.1	9.9	36.0	14.1	7.8	27.3	
Long Term	3. Annual (averaged over 70 years): Worst Case ^a										
	Region 1	0.51	1.6	7.0	1.3	2.5	9.2	3.6	0.57	2.0	
	Region 2	0.46	1.5	6.4	1.2	2.3	8.4	3.3	0.51	1.8	
	Region 3	0.36	1.1	4.9	0.9	1.8	6.5	2.5	0.40	1.4	
	Region 4	0.36	1.2	5.0	0.9	1.8	6.6	2.6	0.40	1.4	
	Region 5	0.46	1.4	6.3	1.2	2.3	8.3	3.2	0.51	1.8	
	Region 6	0.47	1.5	6.5	1.2	2.3	8.5	3.3	0.51	1.9	
	Region 7	0.27	0.9	3.7	0.7	1.4	4.9	1.9	0.31	1.1	
	4. Annual (averaged over 70 years): More realistic ^b										
	Region 1	1.1 E-2	3.4 E-2	0.15	2.7 E-2	5.3 E-2	0.19	7.5 E-2	1.2 E-2	4.3 E-2	
	Region 2	1.0 E-2	3.2 E-2	0.14	2.6 E-2	5.0 E-2	0.18	7.1 E-2	1.1 E-2	4.0 E-2	
	Region 3	0.7 E-2	2.3 E-2	0.10	1.9 E-2	3.6 E-2	0.13	5.2 E-2	8.3 E-3	2.9 E-2	
	Region 4	0.8 E-2	2.5 E-2	0.11	2.0 E-2	4.0 E-2	0.14	5.6 E-2	8.9 E-3	3.1 E-2	
	Region 5	0.9 E-2	2.9 E-2	0.13	2.4 E-2	4.6 E-2	0.17	6.6 E-2	1.0 E-2	3.7 E-2	
	Region 6	1.0 E-2	3.2 E-2	0.14	2.6 E-2	5.0 E-2	0.18	7.1 E-2	1.1 E-2	4.0 E-2	
	Region 7	0.5 E-2	1.7 E-2	0.07	1.4 E-2	2.6 E-2	0.10	3.8 E-2	6.0 E-3	2.0 E-2	

^a Air concentrations adjusted to compensate for emissions for 24 h/day, 4 day/week, 52 week/year over 70 years for Halon 1211 and HCFC 123; a use lifetime of 20 years was assumed for PFH.

^b Air concentrations adjusted to compensate for emissions for 30 min/day, 4 day/week, 52 week/year over 70 years for Halon 1211 and HCFC 123; a use lifetime of 20 years was assumed for PFH.

2. Benzene and Toluene

Maximum ambient air concentrations for benzene and toluene were calculated using the dispersion modeling results at a distance of 500 meters from the source. The emission rates and air concentrations for these two compounds were estimated in the same manner as for the acid gases. Maximum ambient air concentrations ($\mu\text{g}/\text{m}^3$) are shown in Table 34. For the short-term exposures, the ambient air levels are well below the published exposure limits. For benzene, the 1991-1992 ACGIH 8-hour TWA is $0.3 \text{ mg}/\text{m}^3$ and the NIOSH 10-hour TWA is $0.33 \text{ mg}/\text{m}^3$. For toluene, the 8-hour TWA is $377 \text{ mg}/\text{m}^3$, the short-term exposure limit (STEL) is $565 \text{ mg}/\text{m}^3$, and the NIOSH 10-hour TWA is $375 \text{ mg}/\text{m}^3$. The EPA chronic reference dose (RFD) for toluene is $5 \text{ mg}/\text{m}^3$.

The increased cancer risk due to exposure to the benzene emissions ranges from 3.7×10^{-7} (Region 1, worst-case scenario, HCFC 123) to 1.1×10^{-8} (Region 7, worst-case scenario, PFH). For the more realistic long-term scenario, all risk levels are less than 8×10^{-9} .

3. Dioxins and Furans

The increased cancer risk was calculated based on exposure to the dioxins and furans emitted during the training exercises. For each extinguishing agent, the maximum concentration measured during any field test was used, presenting a conservative approach to these calculations. Concentrations of all isomers were converted to 2,3,7,8-TCDD equivalents, using the 1989 revised EPA equivalency factors. For those isomers that were below the detection limits, a concentration equal to the detection limit was assumed. The increased cancer risk, in terms of 2,3,7,8-TCDD equivalents for each extinguishing agent, is presented in Table 35 for each of the seven regions using both worst-case and the more realistic case scenarios. For all extinguishing agents in all regions, the increased cancer risk is less than 8×10^{-8} .

D. SUMMARY

A hypothetical exposure scenario was created to represent the area of maximum exposure based on air dispersion model results and the impacts estimated for a resident at that location. The selected location was 500 meters from the source. Exposure periods of 15 minutes, 8 hours, and 70 years were chosen, representing accepted EPA models, albeit highly conservative. Modeled results were then calculated for each of seven climatic regions of the United States, with Region 1 (Pacific coast) having the highest maximum air concentrations. Region 7 (Atlantic coast) had the lowest maximum concentrations. Increased cancer risks due to benzene, toluene, dioxins, and furans were also calculated and found to be from 3×10^{-7} to 3×10^{-10} .

TABLE 34. MAXIMUM AMBIENT AIR CONCENTRATION OF BENZENE AND TOLUENE (500 METERS FROM SOURCE).

Dispersion Model Scenario		Ambient Air Concentration (µg/m³)					
		Halon 1211		HCFC 123		PFH	
		Benzene	Toluene	Benzene	Toluene	Benzene	Toluene
Short Term	1. Maximum 15-min	0.19	0.52	0.46	0.39	0.09	0.12
	2. Maximum 8-h	0.08	0.21	0.18	0.16	0.04	0.05
Long Term	3. Annual (averaged over 70 years at 30 min/exercise): Worst Case ^a						
	Region 1	1.9 E-2	5.4 E-2	4.5 E-2	4.0 E-2	2.6 E-3	3.4 E-3
	Region 2	1.8 E-2	4.9 E-2	4.1 E-2	3.6 E-2	2.3 E-3	3.1 E-3
	Region 3	1.4 E-2	3.8 E-2	3.2 E-2	2.8 E-2	1.7 E-3	2.6 E-3
	Region 4	1.4 E-2	3.8 E-2	3.2 E-2	2.8 E-2	1.7 E-3	2.6 E-3
	Region 5	1.7 E-2	4.8 E-2	4.0 E-2	3.6 E-2	2.3 E-3	3.1 E-3
	Region 6	1.8 E-2	5.0 E-2	4.2 E-2	3.7 E-2	2.3 E-3	3.1 E-3
	Region 7	1.0 E-2	2.8 E-2	2.3 E-2	2.0 E-2	1.4 E-3	1.7 E-3
	4. Annual (averaged over 70 years at 30 min/exercise): More Realistic ^b						
	Region 1	4.0 E-4	11.3 E-4	9.4 E-4	8.4 E-4	6.4 E-5	2.1 E-5
	Region 2	3.8 E-4	10.6 E-4	8.8 E-4	7.8 E-4	5.1 E-5	6.9 E-5
	Region 3	2.8 E-4	7.7 E-4	6.4 E-4	5.7 E-4	3.7 E-5	4.9 E-5
	Region 4	3.0 E-4	8.4 E-4	7.0 E-4	6.2 E-4	4.0 E-5	5.4 E-5
	Region 5	3.5 E-4	9.8 E-4	8.2 E-4	7.3 E-4	4.6 E-5	6.3 E-5
	Region 6	3.8 E-4	10.6 E-4	8.8 E-4	7.8 E-4	5.1 E-5	6.9 E-5
Region 7	2.1 E-4	5.9 E-4	4.9 E-4	4.4 E-4	2.9 E-5	3.7 E-5	

^a Air concentrations adjusted to compensate for emissions for 24 h/day, 4 day/week, 52 week/year over 70 years for Halon 1211 and HCFC 123; a use lifetime of 20 years was assumed for PFH.

^b Air concentrations adjusted to compensate for emissions for 30 min/day, 4 day/week, 52 week/year over 70 years for Halon 1211 and HCFC 123; a use lifetime of 20 years was assumed for PFH.

TABLE 35. INCREASED LIFETIME CANCER RISK DUE TO
2,3,7,8-TCDD EQUIVALENTS IN EACH REGION.

Dispersion Model Scenario	Extinguishing Agent		
	Halon 1211	HCFC 123	PFH
Worst-Case:			
Region 1	3.5 E-8	7.4 E-8	1.5 E-8
Region 2	3.2 E-8	6.7 E-8	1.4 E-8
Region 3	2.5 E-8	5.2 E-8	1.1 E-8
Region 4	2.5 E-8	5.3 E-8	1.1 E-8
Region 5	3.2 E-8	6.6 E-8	1.4 E-8
Region 6	3.2 E-8	6.8 E-8	1.4 E-8
Region 7	1.9 E-8	3.9 E-8	0.8 E-8
Realistic-Case:			
Region 1	0.7 E-9	1.5 E-9	3.1 E-10
Region 2	0.7 E-9	1.4 E-9	3.1 E-10
Region 3	0.5 E-9	1.1 E-9	2.3 E-10
Region 4	0.6 E-9	1.2 E-9	2.3 E-10
Region 5	0.6 E-9	1.3 E-9	2.9 E-10
Region 6	0.7 E-9	1.4 E-9	3.1 E-10
Region 7	0.4 E-9	0.8 E-9	1.7 E-10

SECTION VI

QUALITY ASSURANCE

All sections of this report were reviewed by appropriately experienced technical staff members in addition to the section authors. A GC/MS specialist, Dr. S. Swanson, audited the volatile data from the Summa® and Tenax®/charcoal samplers and the semivolatile data from the PUF samples. All preparation and analysis records were reviewed for compliance, and selected data were traced back to data on the original sampling records to verify systematic accuracy. The audit reports were submitted to the QA manager and project management on 13 April 1992 (volatiles) and 14 April 1992 (semivolatiles).

The QA manager also conducted a cursory review of the semivolatile and the dioxin/furan analysis records. The samples for dioxin/furan analysis were produced by splitting the semivolatile extractions into two fractions, then performing additional extraction and cleanup.

Problems and corrective actions are discussed below. Because of the problems noted below for the standards and the calibration, the volatile and dioxin/furan data must be reported as "semiquantitative."

A. VOLATILE ANALYSIS

Original sampling records needed for accurate sample identification and sampling parameters were not provided to the analyst before the audit. Instead, a spreadsheet, which summarized the information but contained several errors, was provided. For the audit, the original sampling records were provided to the auditor, who reviewed them with the analyst and resolved several problems. The corrective action needed is to always provide the analyst with hard copies of original sampling records with the samples.

Data transfer errors, from the raw GC/MS data to the analytical summary spreadsheets, were detected and resolved.

Some quality control criteria were not met. On several analysis days, the daily calibration check standard did not meet criteria. In other cases, results were above the calibration curve. Therefore, all results should be reported as "semiquantitative" values.

B. SEMIVOLATILE ANALYSIS

Two sets of semivolatile samples were extracted, but only one set was extracted with a method blank. The missing method blanks for the first set are not considered to be a major problem because the method blank for the second set showed no

contamination, and there was no evidence of field contamination. Thus, no laboratory contamination for the set without a method blank was assumed, but this could not be confirmed. The corrective action needed is to always prepare a method blank for each set of extractions to help confirm lack of laboratory contamination.

The stock solutions used for the calibration were in-date. The stock solutions used for the surrogates exceeded their holding times only by a few weeks. The concentrations should have been acceptable; however, an EPA audit standard or a freshly prepared standard from a different stock was not used to verify these standards, as is required by most EPA procedures. Because the same stock was used for both calibration and spiking, the spiking results are considered to be accurate. The corrective action needed is to always verify all types of standards, calibration, surrogate, and spiking, even if they are in-date, by fresh standards prepared from another stock.

Data transfer problems were noted and resolved, as previously discussed for volatile analysis.

C. DIOXIN/FURAN ANALYSIS

One of two semivolatile extraction method blanks was not prepared, as noted above, for the semivolatile analysis. Because the dioxin/furan samples were obtained as a split of the semivolatile extracts, this lack of one method blank also affected the dioxin/furan analysis. The corrective action is to always prepare a method blank for each set of samples undergoing extraction and cleanup.

Stock standards were out-of-date and were not verified. The results must be reported as semiquantitative. Corrective action required is to (1) not use expired standards, and (2) as a minimum requirement, always analyze a fresh EPA 2,3,7,8-TCDD standard.

D. FTIR DATA

Computerized data included raw spectra, quantitation reports, and Lotus®-processed final data.

An FTIR specialist, T. Long, reviewed the raw spectra listed in Table 36 against the reference spectra and concluded (1) the reference spectra matched the sample spectra, and (2) nothing unusual was detected in the sample spectra. The audit report was submitted to the QA manager on 17 April 1992.

All data calculations performed by the spreadsheet were reviewed and verified by the QA manager, C. Green. No problems were detected except for Run 4, where files FF3R21 and FF3R23 were missing for all compounds, and data for COF₂ for file FF3R19 were missing. The missing COF₂ data were to be determined and entered into the spreadsheet for calculation. The missing runs are explained in the report.

TABLE 36. AUDITED FTIR SPECTRA

Test No.- Spectra File No.	Compound(s)
1-FFIR86	Acetylene
2-FF2R37	HCl, HF, HBr, acetylene, H 1211, COF ₂
3-R2A20	HCl, HF, HBr, acetylene, H 1211, COF ₂
4-FF3R12	HCl, HF, acetylene, Halon 123, COF ₂
5-FF4R9	HCl, HF, acetylene, Halon 123, COF ₂
7-FF6R18	HF, PFH, COF ₂
8-FF7R14	HF, PFH, COF ₂
9-FF8R28	HF, PFH, COF ₂
10-FF9R14	HCl, HF, acetylene, Halon 123, COF ₂

E. OTHER METHODS

The Screening Study vertical profile analyses are included in the volatile analysis section above. The Main Test vertical profile analyses were reviewed by the task leader, G. Scheil, and corrected as necessary. The low Halon 1211 concentrations measured in Run 2 were confirmed when those samples were redone on an electron capture detector. The low concentrations appear to be due to the positioning of the sample probe during this test.

The length of stain tubes are direct reading with no analysis needed. The initial data summary tables were found to have transcription errors, which were recalculated by K. Connery, the final data compiler for this section of the report.

F. SUMMARY

All sections of the report were thoroughly reviewed by appropriately experienced technical staff in addition to the authors. Problems noted with the volatile and dioxin/furan data limit these data to being reported as semiquantitative.

SECTION VII

CONCLUSIONS

1. The FTIR identified an unexpected toxic compound, carbonyl fluoride. When site personnel are exposed to the plume, the compound poses the greatest single threat when they are using any of the other agents.
2. Average total acid gas concentration, as measured by FTIR at the close-in (regular angle) downwind location, showed that IDLH values were exceeded by factors of 7.4 (Halon 1211), 8.1 (HCFC 123), and 9.1 (PFH). Long-angle total acid gas concentrations (single FTIR reading only) showed that IDLH values were exceeded by factors of 3.2, 5.6, and 3.8 (1211, 123, and PFH, respectively). Instantaneous concentrations measured in the plume exceeded the IDLH for COF_2 10 times and the combined IDLH for the total acid gases 20 times.
3. When Halon 1211 was used to extinguish a fire, the four acid gases that were formed (HCl , HBr , HF , COF_2) presented the greatest hazard. Results of modeling indicate that all four gases were near or above their respective IDLH limits at breathing height in the downwind plume at distances of up to 30 meters from the fire. Conservative modeling calculations show that the combined toxicity of all four gases may still be hazardous up to 80 meters downwind.
4. When the two replacement agents, HCFC 123 and perfluorohexane, are used, the respective elimination of HBr and HCl offgases is offset by increases in HF and COF_2 concentrations. Caution should be used in evaluating acid gas exposures based on total acid indicator tubes. Simple acid gas detectors, such as Draeger tubes, give a weak response to carbonyl fluoride and HF , which dominate the toxic emissions from PFH. The apparent reading in a PFH smoke plume may be 3 to 4 times lower than a Halon 1211 smoke plume of equivalent toxicity.
5. For HCFC 123, the modeled individual IDLH limits were exceeded up to a 50-meter distance downwind, and the combined IDLH was exceeded up to 100 meters downwind.
6. For PFH, the modeled individual and combined IDLH values were exceeded at downwind distances up to 100 and 180 meters, respectively. The PFH-modeled results may have been perturbed by the modeling assumptions. Differences between the model and Draeger tube exposures indicate that the perfluorohexane exposure zones should be similar to the other two agents.

7. The FTIR successfully recorded the rapid concentration changes that occur in the plume as firefighting proceeds. During use of all three agents, acid gases, CO, and unburned JP-4 vapor concentrations rise very quickly when agent application begins and then decay over a period of 1 to 5 minutes after agent application ceases.
8. CO, benzene, toluene, JP-4, and the halocarbons were also present at significant levels, but none exceeded the IDLH limits.
9. CO and unburned hydrocarbons increase in concentration as combustion temperature drops when agents are applied to a fire.
10. All three agents showed concentrations up to 100 times greater at ankle height compared to breathing zone height, especially when used to fight a pool fire. Therefore, the agents may reach IDLH limits near ground level.
11. Several polynuclear aromatic hydrocarbons associated with the jet fuel were detected, but not at significant concentrations.
12. Nearly all dioxins were below detection limits. A few furans were detected at low concentrations.
13. Community exposures to dioxins and furans and benzene indicate less than 1×10^{-7} cancer risk.

SECTION VIII

RECOMMENDATIONS

To minimize the risks to firefighters and other exposed individuals, the following items of caution should be considered:

1. Because all known halocarbon extinguishing agents will produce mixtures of toxic acid gases whenever they are applied to a flame or high temperature source, their use must be carefully evaluated in any situation where the resulting plume may expose unprotected persons.
2. Halocarbon-based agents should not be used by untrained personnel.
3. Discharging halocarbon-based extinguishers in such a manner that the resulting plume may envelop unprotected personnel, especially if such persons have no easy exit available, is to be avoided.
4. Because acid-gas concentrations are highest in the plume, adjacent to it, and downwind from it during the extinguishant application and for a few minutes afterwards, these toxic-hazard areas should be avoided by personnel who do not have breathing protection.
5. When using halocarbon-based extinguishants, personnel should note wind direction prior to use and attack the fire from the upwind direction, where the least chance of exposure to the plume gases will occur.
6. Firefighters should be informed that the acid gas plume from the application of PFH to a fire is much less visible but just as toxic as Halon 1211. Plume visibility using HCFC 123 is intermediate between the other two agents.
7. Whenever possible, personnel who may be exposed to the extinguisher/smoke plume should wear a pressure-demand, supplied-air respirator.
8. Because all three agents tested are much denser than air and concentrate near ground level, asphyxiation from the neat agents is possible near ground level, especially in low-lying areas.

APPENDIX A

SCREENING STUDY

The original planned test matrix is shown in Table A-1. The final test set required one additional fuel-only test for setting up the FTIR and a repeat of the full fuel-only test due to sampler problems and an excessive amount of fuel, which resulted in a very intense, long burning fire. Table A-2 shows the test conditions during each test. The project archives include video tapes from various angles of each test.

A. RESULTS

1. VOCs

The Screening Study required (a) an investigation of the significant species, including VOCs, present at various sampling locations and (b) an evaluation of sampling and analysis methods in preparation for the subsequent Main Test. For the VOC characterization, the sampling devices included Summa[®] canisters and two types of adsorbent traps, Tenax[®] and Carbosieve[®]. Because very volatile organic compounds (such as chloromethane) are not retained effectively by Tenax[®] adsorbents, a backup trap containing Carbosieve[®] adsorbent also was used in series with the Tenax[®] trap. VOCs collected by both Summa[®] and Tenax[®]/Carbosieve[®] sampling methods were quantitatively determined for a number of "target" organic compounds selected prior to the Screening Study. These target analytes were chosen based on a list of candidate VOCs provided by the Air Force, the likelihood of formation during combustion, and compatibility with the analytical methods employed. In addition, a semiquantitative measure of the tentatively identified compounds (TICs) present in each sample was provided by searching the analytical data files after the initial analysis.

VOC results by the three sampling methods (Tenax[®], Carbosieve[®], and Summa[®]) were obtained from the runs 4, 5, and 6. In Run 4, which was a special experiment using JP-4 and Halon 1211, Summa[®] canisters collected samples at three vertical heights adjacent to the firefighter to provide a "vertical profile." In Runs 5 and 6, which consisted of Halon 1211 and JP-4 (only) conditions, respectively, all three sampling methods were used in both the firefighter's breathing area and the plume. In addition, several method and field blanks consisting of canisters and adsorbent traps accompanying the sampling event were collected.

TABLE A-1. PLANNED SCREENING STUDY TEST MATRIX.

Test condition	Type	Sampling methods	Number of samples	Sample location	Analytical methods
1	Fuel only	FTIR	N/A	Plume	Data reduction
2	Fuel only	Summa® PUF Tenax®/CMS CO monitor FTIR	2 2 2 N/A N/A	Plume,FF Plume,FF Plume,FF Plume,FF Plume	GC/MS GC/MS GC/MS NDIR continuous monitor Data reduction
3	Fuel plus agent	Summa® FTIR	3 (vertical profile) Temperature profile	FF Fire	GC/MS Blackbody radiation curve
4	Fuel plus agent	Summa® PUF Tenax®/CMS CO monitor FTIR	2 2 2 N/A N/A	Plume,FF Plume,FF Plume,FF Plume,FF Plume	GC/MS GC/MS GC/MS NDIR continuous monitor Data reduction

FF = Firefighter level

FTIR = Fourier Transform Infrared Analyzer

PUF = Polyurethane Foam Sampler

CMS/Tenax® = Tenax®/Carbon Molecular Sieve Sampler (also called Tenax®/Carbosieve®)

CO = Carbon Monoxide Monitor

GC/MS = Gas Chromatography/Mass Spectrometry

NDIR = Non-dispersive Infrared Analyzer

TABLE A-2. SCREENING STUDY FIELD TEST CONDITIONS.

Test No.	1	2	3 ^a	4	5	6
Date	7/30/91	7/30/91	7/30/91	7/31/91	7/31/91	8/1/91
Time of day	9 a.m.	10 a.m.	11:30 a.m.	10 a.m.	11 a.m.	8:30 a.m.
Winds, direction, speed (mph)	Calm	SSW, 1-5	SSW, 1-15	SSW, 1-5	SSW, 1-5	Calm
Fuel amount (gal)	12	12	120.7	15.6	15.6	25
Fire duration (min)	2	2	20	2 (fire extinguished)	2 (fire extinguished)	5
Agent type	None	None	None	Halon 1211	Halon 1211	None
Types of samples	FTIR	FTIR	ALL	FTIR, vertical profile	ALL	ALL

^a Test aborted, samples not analyzed.

All of the test conditions in the Screening Study involved the use of jet fuel (JP-4). The VOCs attributable to JP-4 consisted of a complex mixture of hydrocarbons (HCs). Since the nonaromatic JP-4 HCs are generally considered to be less of a health concern, only the aromatic compounds attributable to JP-4 (including benzene and toluene) were included as target analytes for quantitative determination. A list of target analytes chosen for the Screening Study is given in Table A-3.

The method detection limits (MDLs) and the concentration ranges attainable by using Summa[®] canisters and Tenax[®]/Carbosieve[®] methods are summarized in Table A-4. The Summa[®] canister method provided a much wider quantitative concentration range than the adsorbent trap methods because multiple analyses are possible from the same canister. The Summa[®] canister method provided a quantitative concentration range of roughly 5 ppb (by volume) to 30,000 ppb. The Tenax[®] adsorbent trap method, on the other hand, which achieves lower MDLs, provided a quantitative concentration range of roughly 0.2 ppb to 50 ppb. For very volatile organic compounds, the Carbosieve[®] adsorbent traps provided a quantitative concentration range of 0.1 ppb to 800 ppb.

a. Run 6 (JP-4 only)

GC/MS data acquired in full-scan mode allowed a quantitative measure of target compounds and characterization of other non-target compounds to be made. One type of graph obtained from GC/MS analysis is a RIC (Reconstructed Ion Chromatogram) that displays an overall measure of the sample components as separated by retention time (x-axis) and their respective abundances (y-axis). Figure A-1 shows example RICs for samples taken by the Summa[®] canister, Tenax[®], and Carbosieve[®] in the firefighter's breathing zone for Run 6 (jet fuel-only). The jet fuel-only (Run 6) test gives a RIC that shows a complex chromatogram made up of many hydrocarbon compounds. Notice that the Summa[®] and Tenax[®] chromatograms are similar, except for early eluting compounds where "breakthrough" for the Tenax[®] sampler is evident by the absence of several peaks in the Tenax[®] RIC. The Carbosieve[®] adsorbent sampler, on the other hand, effectively retains very volatile compounds.

Figure A-2 shows RICs for samples taken by the Summa[®] canister, Tenax[®], and Carbosieve[®] from the plume for Run 6 (jet fuel-only). Again, the Tenax[®] sampler shows significant "breakthrough" of early eluting compounds.

A summary of the target analyte concentrations (ppb) for all Run 6 samples collected and analyzed is presented in Table A-5. For cases where the initial analyses of the Summa[®] canisters exceeded the calibration range of the GC/MS system, a smaller volume of sample from the canister was analyzed to provide a more accurate concentration.

TABLE A-3. VOC TARGET ANALYTES FOR THE
SCREENING STUDY.

Summa® Analysis

Target analytes

Chloromethane
1,3-Butadiene
Halon 1211
Benzene
Toluene

Surrogates

Spiked at 50 ng/adsorbent trap
*d*₈-Toluene
Bromofluorobenzene

Internal standards

Spiked at 50 ng/adsorbent trap
1,4-Difluorobenzene
*d*₅-Chlorobenzene

Tenax® Analysis

Target analytes

1,3-Butadiene
Halon 1211
1,1,1-Trichloroethane
Carbon tetrachloride
Benzene
Trichloroethene
Toluene
Tetrachloroethene
Ethylene dibromide
p-Xylene
JP-4

Surrogates and internal standards

Sample as Summa analysis

Carbosieve® III Analysis

Target analytes

1,3-Butadiene
Halon 1211

Internal standard

Spiked at 50 ng/adsorbent trap
Chloromethane

TABLE A-4. METHOD DETECTION LIMITS (MDLs) AND CONCENTRATION RANGES FOR VOC SAMPLES
(Concentration, ppb).

Analyte	Sampling method:		Tenax		Carbosieve		Summa	
	Min	Max	Min	Max	Min	Max	Min	Max
Chloromethane	*	*	*	*	*	*	72	3,600.00
1,3-Butadiene	0.32	56	1.12	279	6.7	3,300.00		
Halon 1211	0.138	24.1	0.048	880	2.89	28,900.00		
1,1,1-Trichloromethane	0.145	25.3	*	*	*	*		
Carbon tetrachloride	0.112	19.6	*	*	*	*		
Benzene	0.221	39	*	*	4.6	2,320.00		
Trichloroethene	0.131	23	*	*	*	*		
Toluene	0.187	33	*	*	3.9	1,960.00		
Tetrachloroethene	0.104	18.1	*	*	*	*		
Ethylene dibromide	0.094	16.4	*	*	*	*		
p-Xylene	0.162	28.4	*	*	*	*		

* = not included in curve.

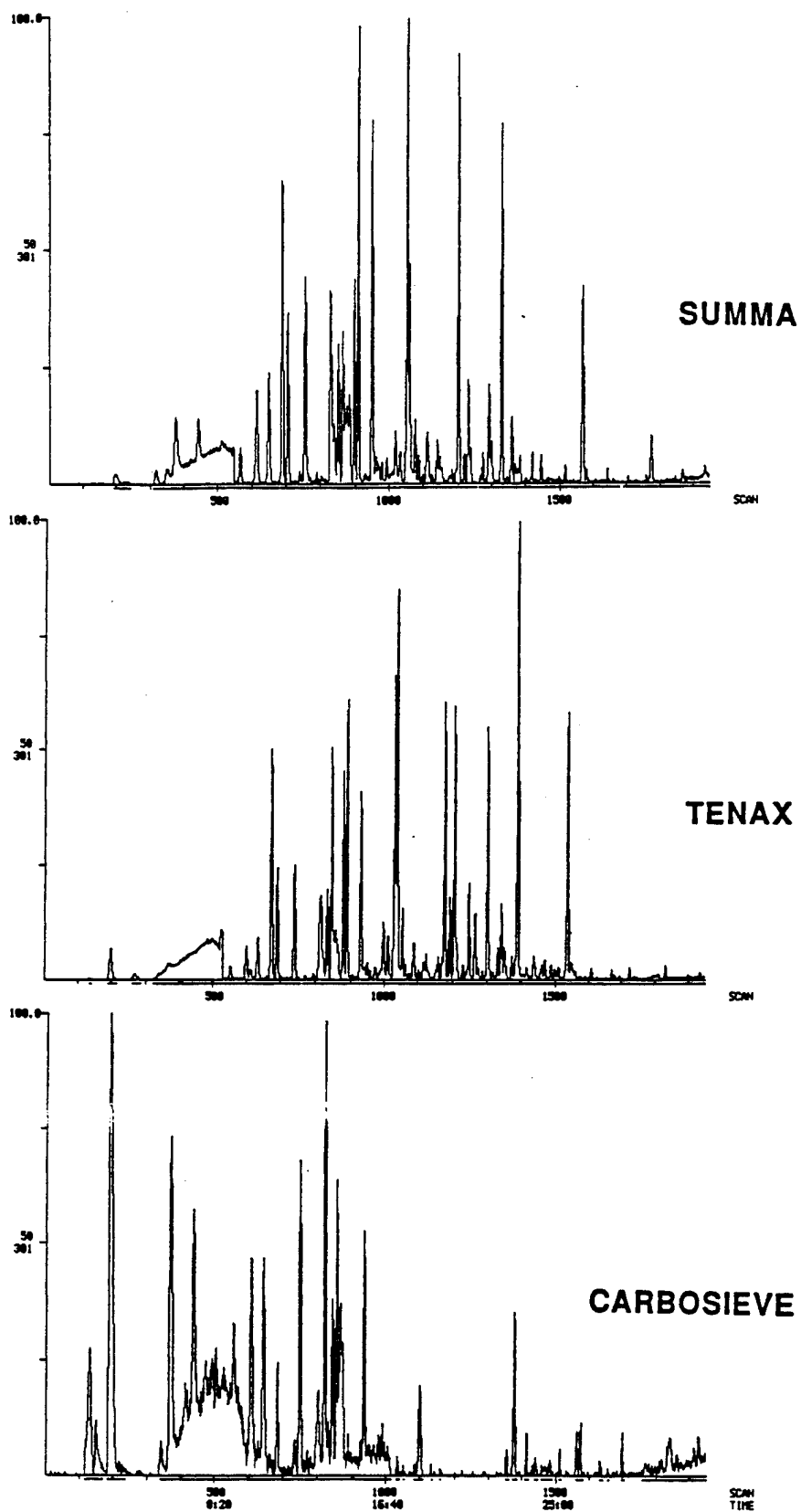


Figure A-1. Example RICs for Summa[®], Tenax[®], and Carbosieve[®] samples collected in the firefighter's breathing zone (Run 6, JP-4 only).

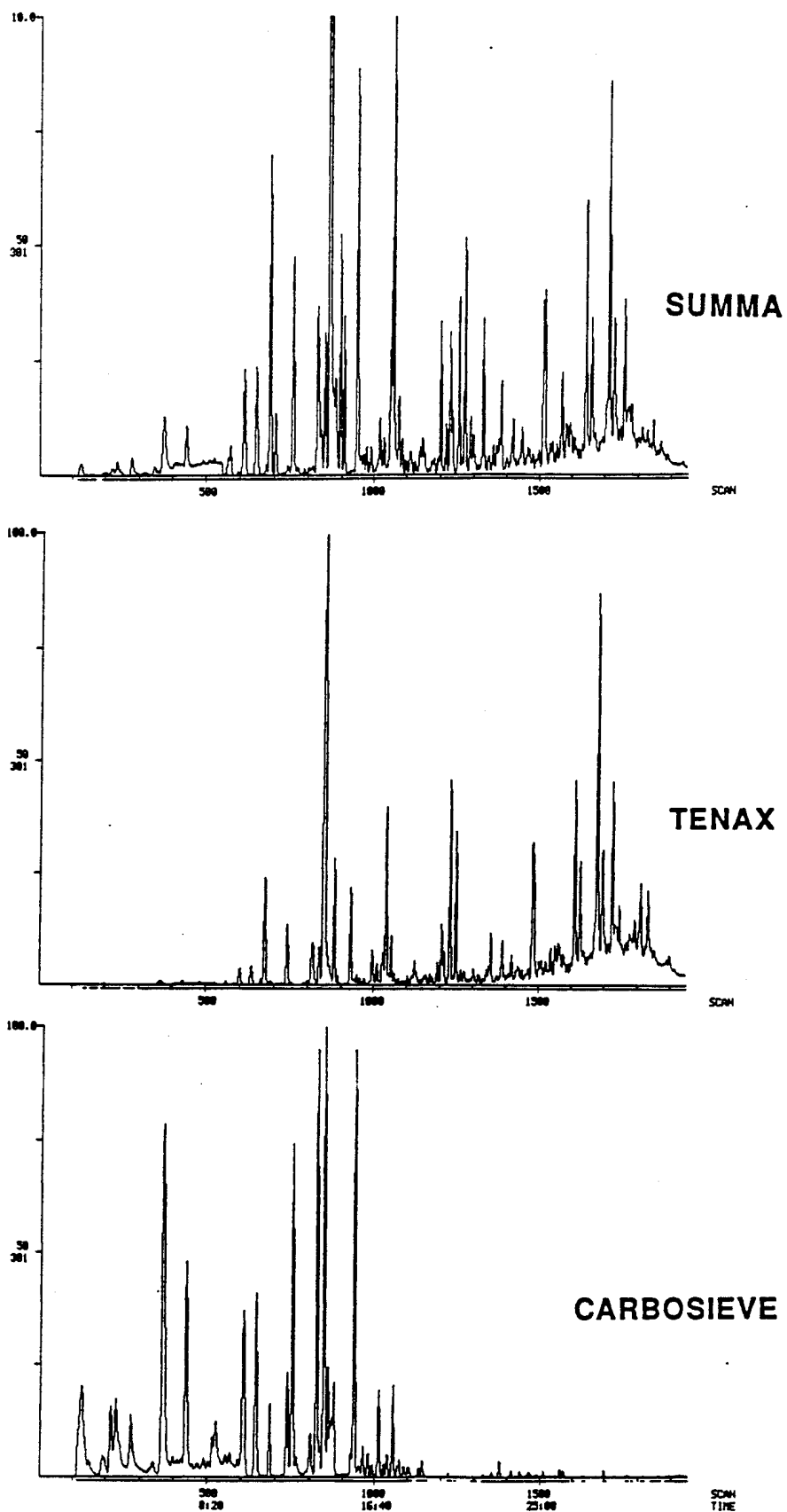


Figure A-2. Example RICs for Summa®, Tenax®, and Carbosieve® samples collected in the plume (Run 6, JP-4 only).

TABLE A-5. VOC RESULTS (TEST 6, JP-4 ONLY)
(Concentration ppb by volume).

Sample type:			Firefighter		Plume		
Sampling method:	Tenax ^{®a}	Carbosieve [®]	Summa [®]	Tenax [®]	Carbosieve [®]	Summa [®]	
Sample No:	3030	3031	3014	3028	3029	3013	
Target analyte							
Chloromethane	*	*	-	*	*	-	
1,3-Butadiene	-	-	-	-	14.3	94	
Halon 1211	-	trace	-	-	9.2	30	
1,1,1-Trichloromethane	trace	*	*	trace	*	*	
Carbon tetrachloride	trace	*	*	trace	*	*	
Benzene	10.7	*	44	1,900	*	4,700	
Trichloroethene	-	*	*	-	*	*	
Toluene	17.3	*	61	166	*	330	
Tetrachloroethene	-	*	*	-	*	*	
Ethylene dibromide	-	*	*	-	*	*	
p-Xylene	10.3	*	*	30	*	*	
JP-4 ^a	170	*	*	940	*	*	

^a JP-4 calculations were based on the gc/ms response of 5 of its major constituents. The concentrations reported should be used as estimates only.

Trace = < 1 ppb.

(-) = Not detected.

(*) = Target was not quantitated in this sample.

b. Run 5 (Halon 1211)

Figure A-3 shows the RICs for the Summa[®] canister, Tenax[®], and Carbosieve[®] samples collected from the firefighter's breathing area for Run 5 utilizing Halon 1211 as the extinguishing agent. Since a complete capture of VOCs was accomplished with the Summa[®], it is evident from the Tenax RIC (Figure A-3b) that severe "breakthrough" for Halon 1211 occurred.

Figure A-4 shows the RICs for the Summa[®] canister, Tenax[®], and Carbosieve[®] samples collected from the plume for Run 5 utilizing Halon 1211 as the extinguishing agent. Again, Halon 1211 breakthroughs for both the Tenax[®] and Carbosieve samplers are evident. The other peaks in the RIC are attributable to the JP-4.

A summary of target analyte concentrations (ppb) for Run 5 is given in Table A-6. As expected, the greatest exposure was seen during use of the Halon 1211 agent with concentrations of 34,000 ppb being observed.

c. Run 4 (Vertical Profile)

For Run 4 (Halon 1211 "vertical profile"), Summa[®] canister samples were collected at three vertical heights; breathing height (face), waist height, and ankle height, 6 inches above the ground. Figure A-5 shows the RICs for Summa[®] canister analysis corresponding to the ground, waist, and breathing height locations. As expected, Halon 1211, being heavier than air, was more concentrated near the ground.

A summary of the concentrations for the target analytes for Run 4 is given in Table A-7. For comparison purposes, a smaller sample volume from the Summa[®] canister (50 mL) was analyzed to extend the dynamic calibration range analysis of the high levels of Halon encountered. In general, the 50-mL sample agreed well with the initial 1-liter analysis.

d. Runs 4, 5, and 6—Tentatively Identified Compounds (TICs)

The TICs observed for each test condition are given in Table A-8. Identification of these compounds is based on comparisons to library reference mass spectra and manual inspection. Concentrations of the TICs are based on the responses relative to the internal standards. More accurate quantitation for the TICs is possible only by the analysis of authentic standards, which was beyond the scope of this work.

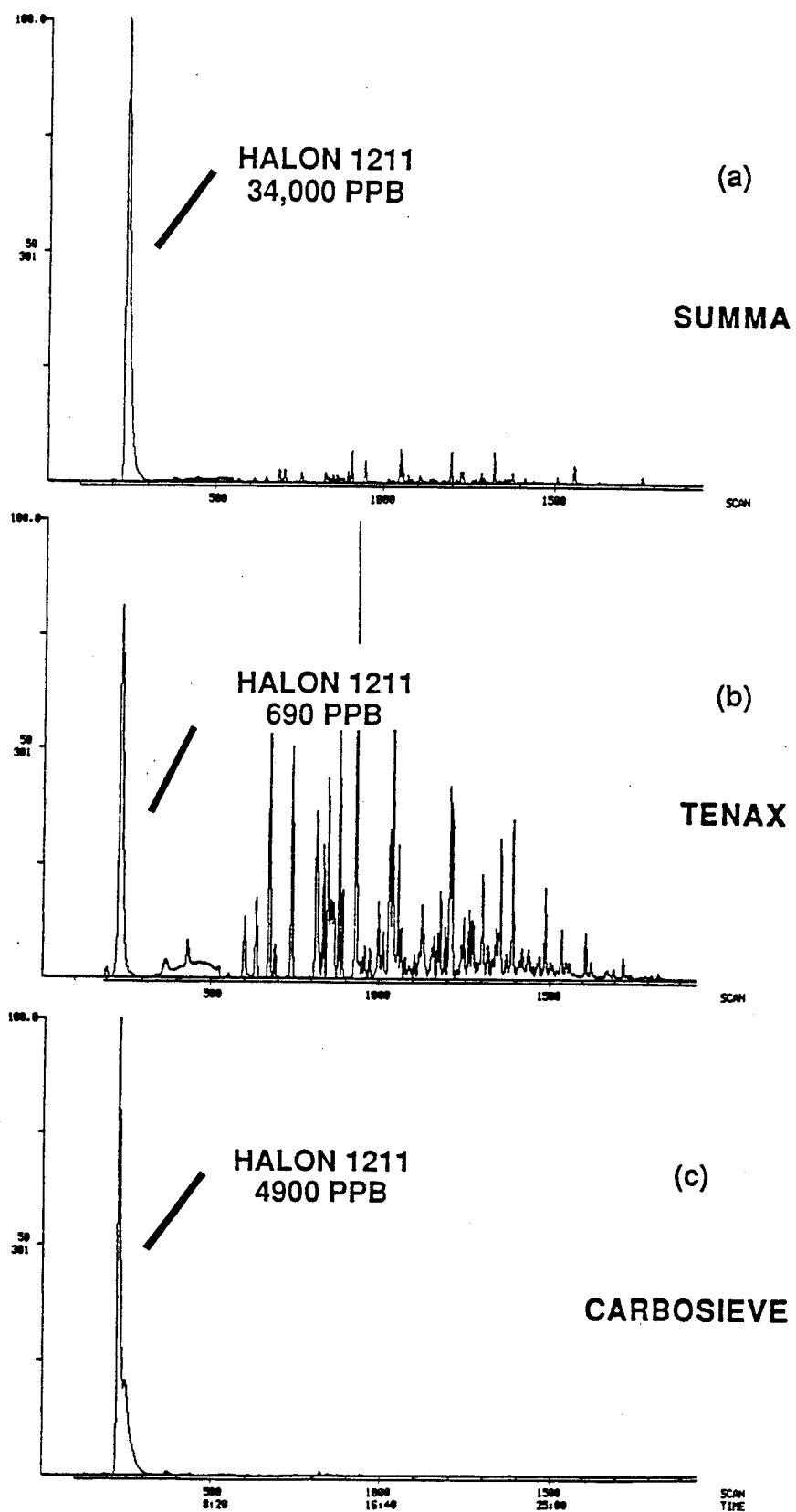


Figure A-3. Example RICs for Summa®, Tenax®, and Carbosieve® samples collected at firefighter's breathing area (Run 5, Halon 1211).

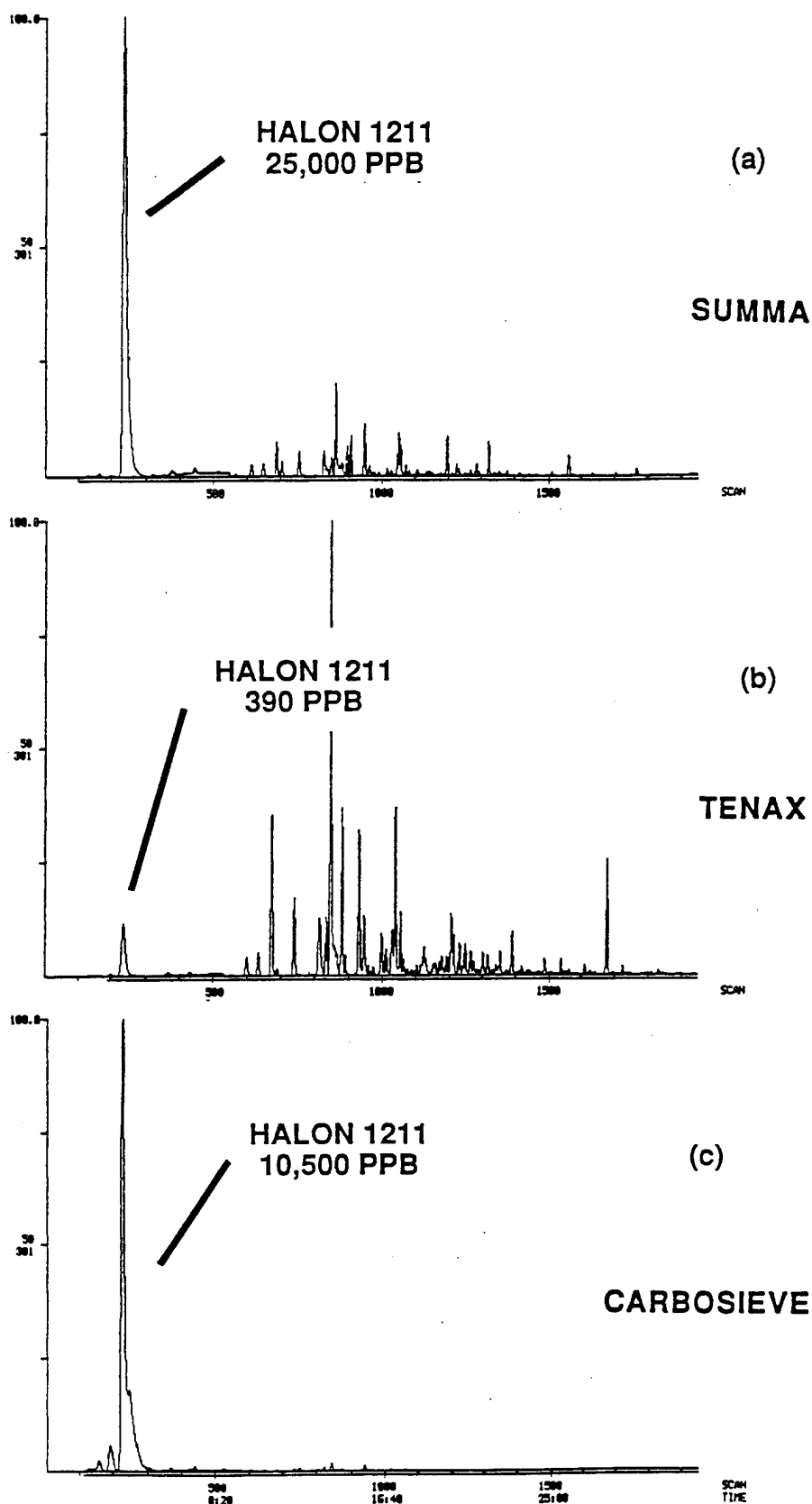


Figure A-4. Example RICs for Summa®, Tenax®, and Carbosieve® samples collected in the plume (Run 5, Halon 1211).

TABLE A-6. SUMMARY OF VOC CONCENTRATIONS FOR RUN NO. 5 (Halon 1211)
(Concentration ppb by volume).

Sample type:	Firefighter			Plume		
	Tenax ^{®a}	Carbosieve [®]	Summa [®]	Tenax [®]	Carbosieve [®]	Summa [®]
Sample No:	2030	2031	2019	2028	2029	2013
Target analyte						
Chloromethane	*	*	-	*	-	-
1,3-Butadiene	-	-	-	-	12.4	-
Halon 1211	690	4,900	34,000	390	10.5	25,000
1,1,1-Trichloromethane	trace	*	*	trace	*	*
Carbon tetrachloride	-	*	*	trace	*	*
Benzene	47	*	42	570	*	430
Trichloroethene	-	*	*	-	*	*
Toluene	70	*	69	160	*	137
Tetrachloroethene	-	*	*	-	*	*
Ethylene dibromide	-	*	*	-	*	*
p-Xylene	35	*	*	44	*	*
JP-4 ^a	2,520	*	*	3,100	*	*

^a JP-4 calculations were based on the gc/ms response of 5 of its major constituents. The concentrations reported should be used as estimates only.

Trace = < 1 ppb.

(-) = Not detected.

(*) = Target was not quantitated in this sample.

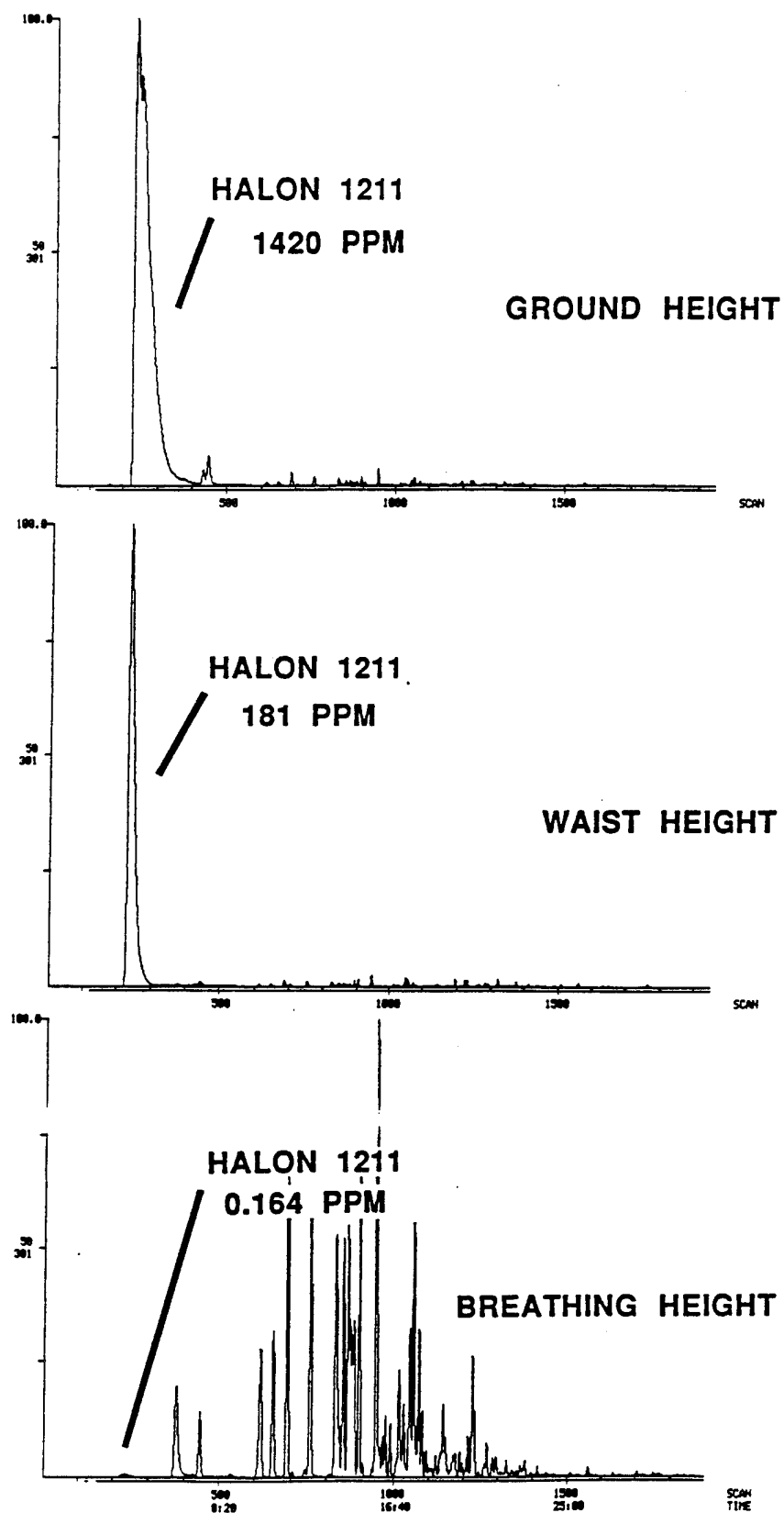


Figure A-5. Example RICs of Summa® samples for vertical profile experiment (Run 4, Halon 1211).

2. Semivolatile Organics (SVOs)

Firefighter and community exposure to SVOs released during firefighter training exercises was measured by collecting samples with PUF adsorbent cartridges followed by solvent extraction and GC/MS analysis. Quantitative determination was performed on a number of target SVO analytes selected prior to the Screening Study. These targets were chosen, based on a list of candidate SVOs provided by the Air Force, the likelihood of their presence in the combustion process, and their compatibility with the analytical methods employed. In addition, a semiquantitative measure of TICs was provided by searching the analytical data files after initial analysis.

SVO results were obtained from two separate locations for Runs 5 and 6: the firefighter's breathing zone and the plume. Particulate filters and probe rinse samples were also collected for analysis. The PUF cartridges were analyzed individually, while the filter and probe rinses were combined for analysis. Additionally, blank filters and cartridges were also analyzed. A list of the SVO target analytes chosen for the Screening Study is given in Table A-9.

All of the Screening Study test conditions utilized jet fuel (JP-4) for the test fire. The SVOs attributable to JP-4 consisted of a complex mixture of hydrocarbons, including phenol and polyaromatic hydrocarbons (PAHs). Almost all of the SVO target analytes chosen for this study originate from the JP-4 fuel.

The method detection limits (MDLs) for the selected SVO methods are summarized in Table A-10. The methods used provided a quantitative measure of SVO concentrations ranging from 13 $\mu\text{g}/\text{m}^3$ to 310 $\mu\text{g}/\text{m}^3$.

Figures A-6 and A-7 show RICs for samples collected by the PUF cartridge and filter/probe rinse in the firefighter's breathing zone for Runs 6 and 5, respectively. These samples did not contain any of the target analytes above the MDL. The majority of the peaks evident in the RIC consist of either surrogates or internal standards used in GC/MS analysis.

Figures A-8 and A-9 show RICs for the plume PUF cartridges and filter/rinses from Runs 6 and 5, respectively. The majority of the chromatographic peaks displayed originate from JP-4 and consist of a complex mixture of hydrocarbons and PAHs. In Run 6, the filter/rinse sample extract contains the greater number of components, some of which are included in the SVO target analyte list. A summary of the SVO target analyte concentrations for Run 6 (jet fuel only) and Run 5 (Halon 1211) is presented in Table A-11. In general, very low levels were measured.

TABLE A-7. SUMMARY OF VOC CONCENTRATIONS FOR VERTICAL PROFILE EXPERIMENT
(RUN 4, HALON 1211)
(Concentration ppb by volume).

Target compound	Sample type: FF Summa®		FF Summa®		FF Summa®	
	Sampling position: High		Mid		Low	
Sample No.:	2,014		2,015		2,016	
Analysis volume:	50 mL	1.00 L	50 mL	1.00 L	50 mL	1.00 L
Target compound						
Chloromethane	-	-	-	-	-	-
1,3-Butadiene	-	-	-	91	-	-
Halon 1211	77	164	270,000	181,000	2,920,000	1,420,000
Benzene	1,180	1,460	169	85	680	236
Toluene	1,370	2,080	225	152	1,500	350

(-) = Not detected.

TABLE A-8. TICs (TENTATIVELY IDENTIFIED COMPOUNDS)
OBSERVED IN RUNS 4, 5, AND 6.

Dichlorodifluoromethane
Dichlorofluoromethane
Dibromomethane
Ethynylbenzene
Ethenylbenzene
(Styrene)
Propynylbenzene

TABLE A-9. SVOC TARGET ANALYTES FOR PUF SAMPLES—
SCREENING STUDY.

Target analytes

Standard curve concentrations: 20, 50, and 200 ng/μL

1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
Nitrobenzene
Hexachlorobenzene
Hexachloroethane
Phenol
4-Bromophenyl(phenyl) ether
Acenaphthene
Acenaphthylene
Anthracene
Benz[*a*]anthracene
Benzo[*a*]pyrene
Benzo[*b*]fluoranthene
Benzo[*k*]fluoranthene
Benzo[*g,h,i*]perylene
Chrysene
Dibenz[*a,h*]anthracene
Fluoranthene
Fluorene
Indeno[1,2,3-*cd*]perylene
Naphthalene
Phenanthrene
Pyrene

Surrogates

Spiked at 80 μg/PUF or filter sample

*d*₅-Nitrobenzene
*d*₄-1,2-Dichlorobenzene
*d*₁₄-Terphenyl

Internal standards

Spiked at 40 μg/mL of GC/MS sample

*d*₁₀-Acenaphthalene
*d*₁₂-Chrysene
*d*₈-Naphthalene
*d*₁₀-Phenanthrene

TABLE A-10. METHOD DETECTION LIMITS (MDLS)
FOR SVO COMPOUNDS.

SVO target analytes	MDL ($\mu\text{g}/\text{m}^3$)
1,3-Dichlorobenzene	20
1,4-Dichlorobenzene	20
1,2-Dichlorobenzene	20
Nitrobenzene	20
Hexachloroethane	20
Phenol	20
4-Bromophenyl(phenyl)ether	20
Acenaphthene	20
Acenaphthylene	20
Anthracene	20
Benz[a]anthracene	20
Benzo[a]pyrene	20
Benzo[b]fluoroanthene	20
Benzo[k]fluoroanthene	20
Benzo[g,h,i]perylene	20
Chrysene	20
Dibenzo[a,h]anthracene	20
Fluoranthene	20
Fluorene	20
Indeno[1,2,3-cd]perylene	20
Naphthalene	20
Phenanthrene	20
Pyrene	20

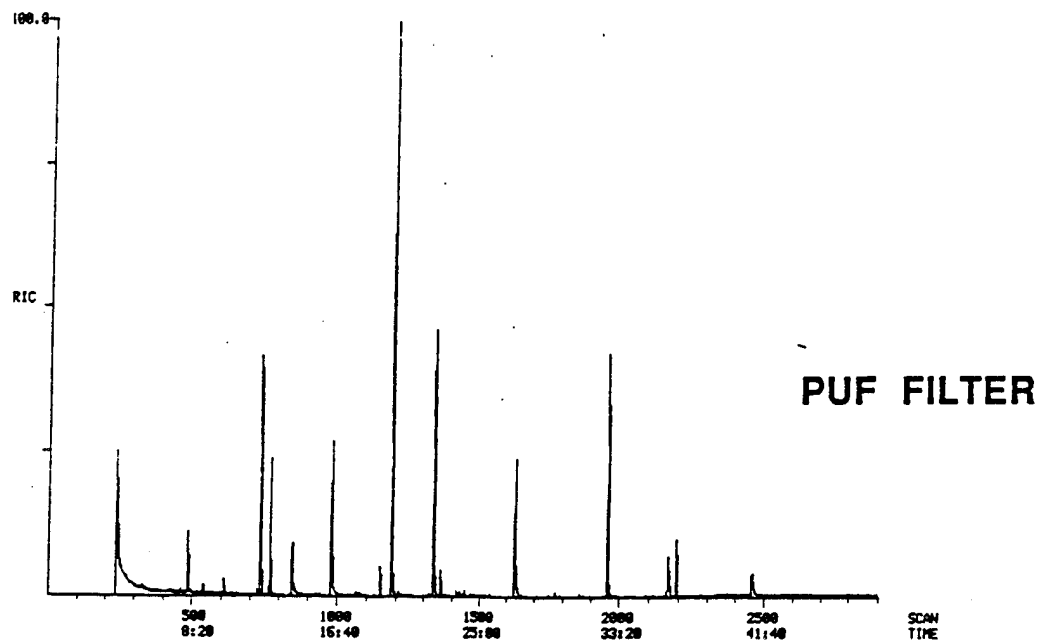
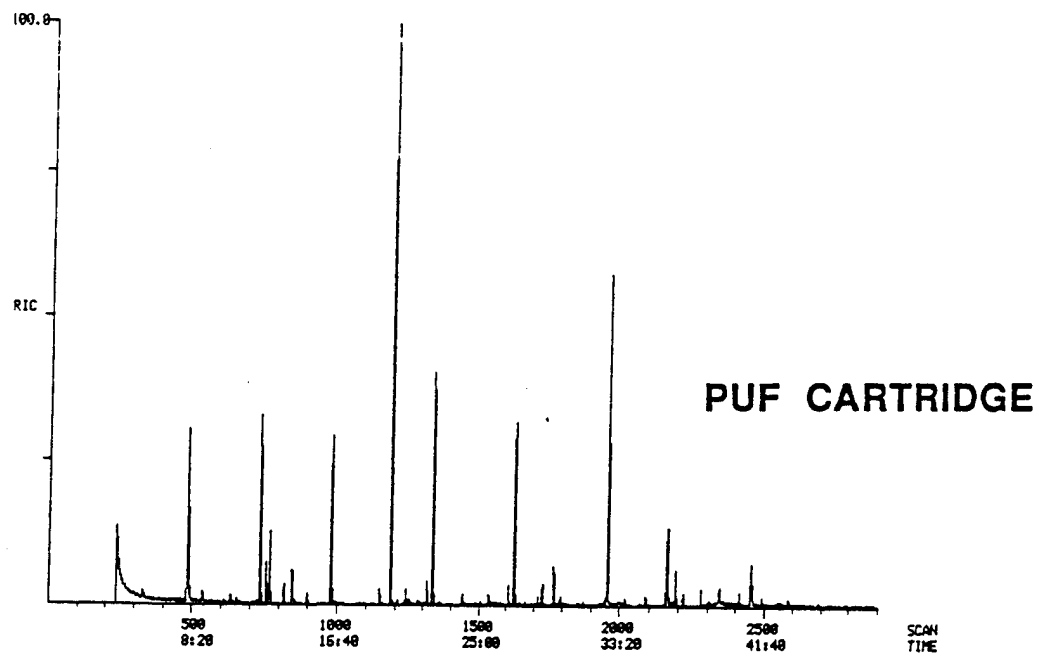


Figure A-6. Example RICs of SVOs from firefighter's breathing zone (Run 6, JP-4 only).

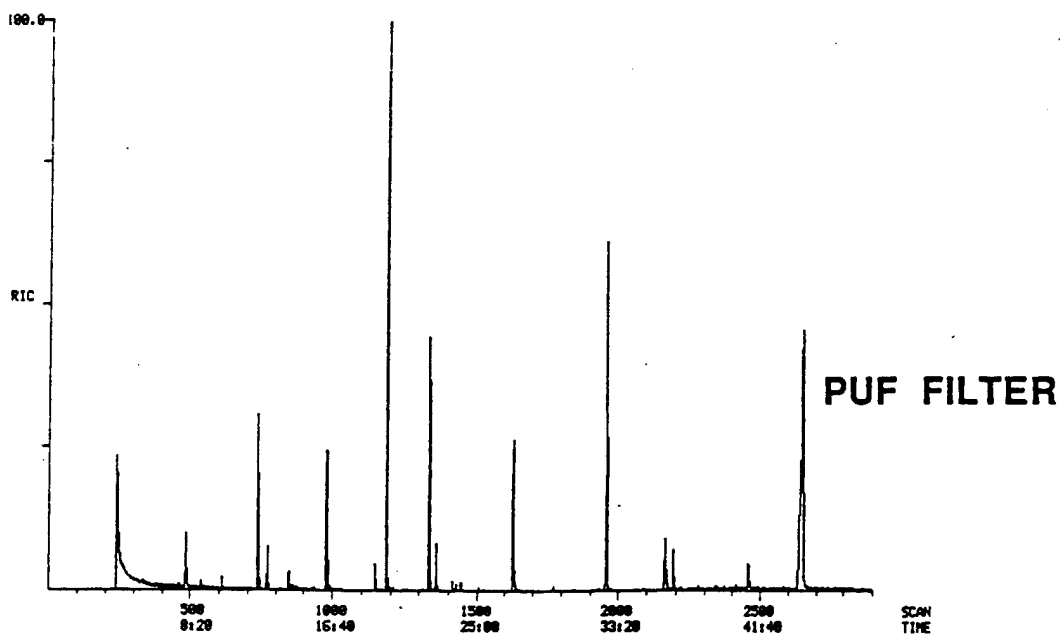
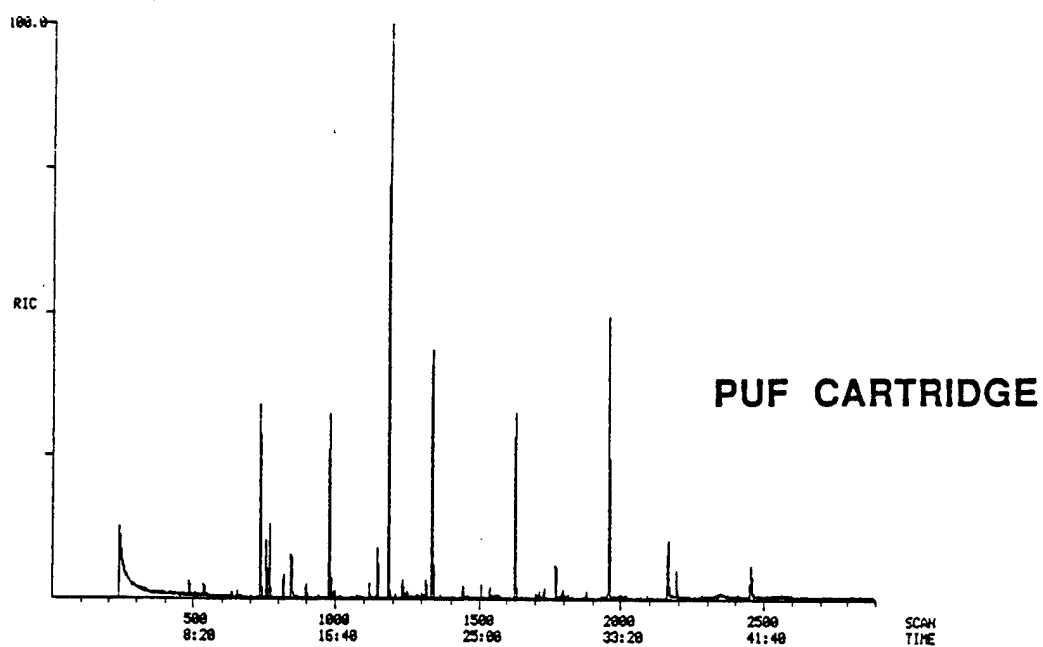


Figure A-7. Example RICs of SVOs from firefighter's breathing zone (Run No. 5, Halon 1211).

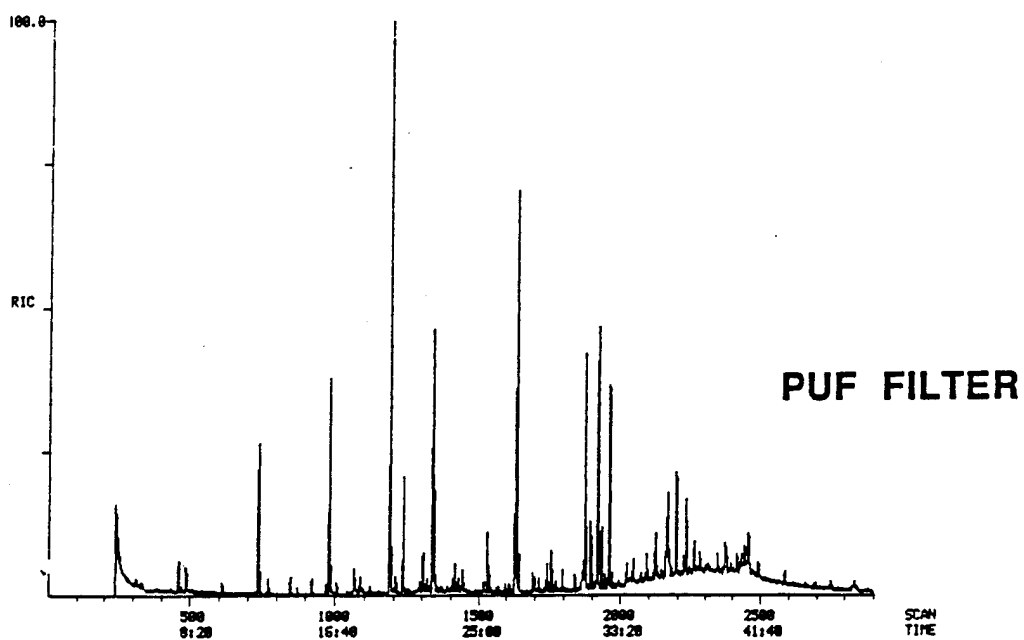
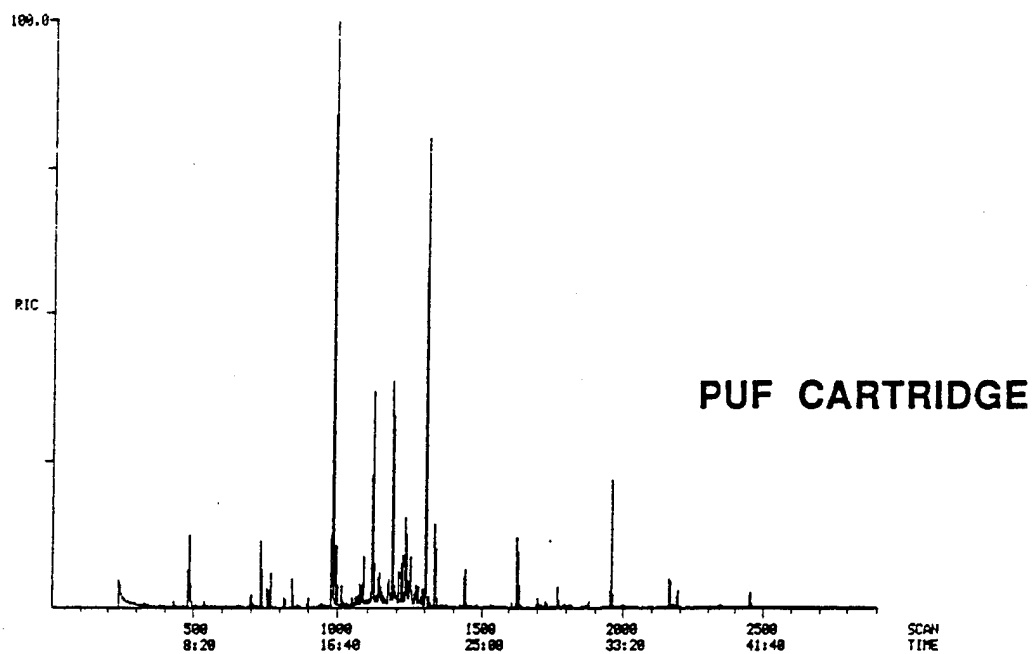


Figure A-8. Example RICs of SVOs from the plume (Run 6, JP-4 only).

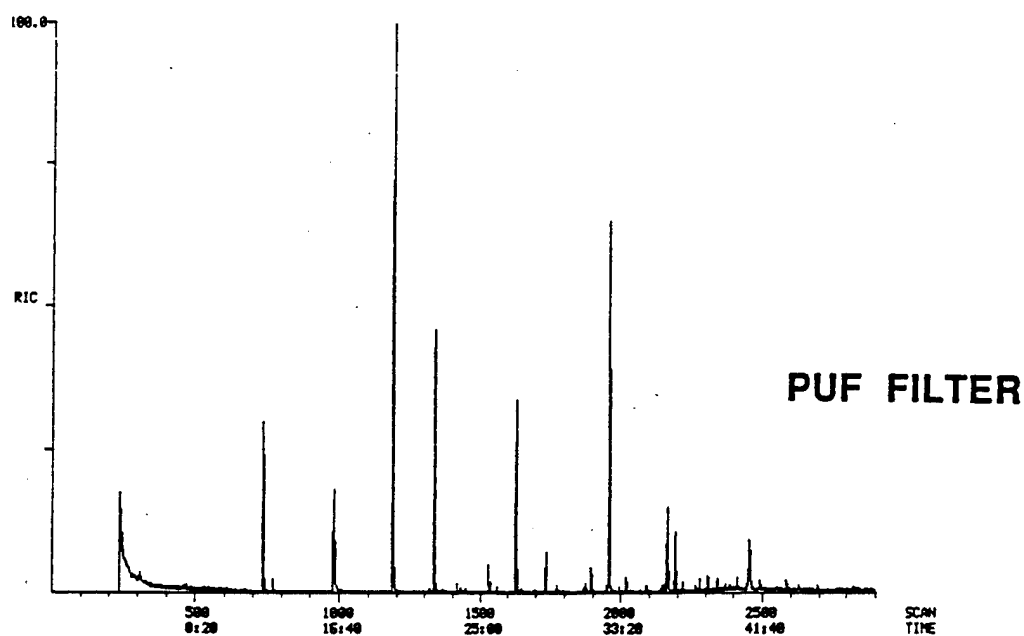
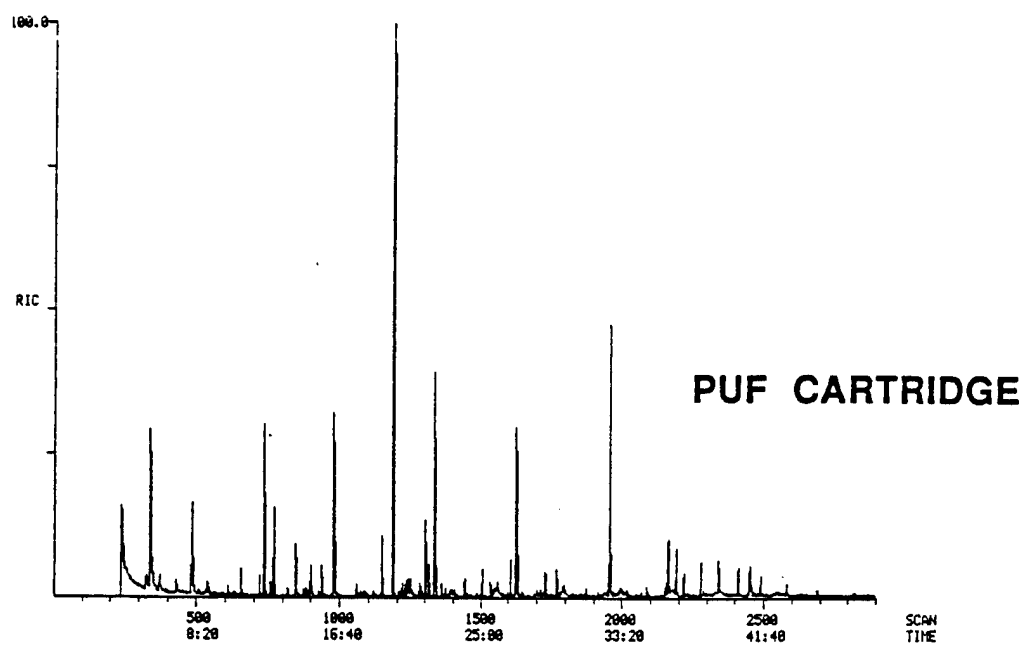


Figure A-9. Example RICs of SVOs from the plume (Run 5, Halon 1211).

TABLE A-11. SUMMARY OF SVO TARGET ANALYTE CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)
FOR RUN 6 (JP-4 ONLY) AND RUN 5 (HALON 1211)

Target compound	RUN 5						RUN 6					
	FF			PLUME			FF			PLUME		
	PUF cart.		PUF filter	PUF cart.		PUF fill/rinse	PUF cart.		PUF filter	PUF cart.		PUF fill/rinse
	2006	2007	2007	2003	2004	2004	3006	3007	3007	3003	3004	3004
1,3-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
1,4-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
1,2-Dichlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
Nitrobenzene	-	-	-	-	-	-	-	-	-	-	-	-
Hexachlorobenzene	-	-	-	-	-	-	-	-	-	-	-	-
Hexachloroethane	-	-	-	-	-	-	-	-	-	-	-	-
Phenol	-	-	-	-	-	-	-	-	-	< 20	-	-
4-Bromophenyl(phenyl) ether	-	-	-	-	-	-	-	-	-	-	-	-
Acenaphthene	-	-	-	-	-	-	-	-	-	< 20	-	-
Acenaphthylene	-	-	-	< 31	-	-	-	-	-	119	< 20	< 20
Anthracene	-	-	-	< 31	-	-	-	-	-	< 20	< 20	< 20
Benz[a]anthracene	-	-	-	-	< 31	-	-	-	-	-	< 20	< 20
Benz[a]pyrene	-	-	-	-	-	-	-	-	-	-	< 20	< 20
Benz[b]fluoranthene	-	-	-	-	-	-	-	-	-	-	< 20	< 20
Benz[k]fluoranthene	-	-	-	-	< 31	-	-	-	-	-	< 20	< 20
Benz[g,h,i]perylene	-	-	-	-	-	-	-	-	-	-	< 20	< 20
Chrysene	-	-	-	-	-	-	-	-	-	-	< 20	< 20
Dibenz[a,h]anthracene	-	-	-	-	-	-	-	-	-	-	-	-
Fluoranthene	-	-	-	-	< 31	-	-	-	-	< 20	34	< 20
Fluorene	-	-	-	< 31	-	-	-	-	-	< 20	< 20	< 20
Indeno[1,2,3-cd]pyrene	-	-	-	< 31	-	-	-	-	-	-	< 20	< 20
Naphthalene	< 31	-	-	< 31	-	-	-	-	-	145	-	-
Phenanthrene	< 31	-	-	< 31	-	-	< 20	-	-	< 20	36	< 20
Pyrene	-	-	-	< 31	< 31	-	-	-	-	-	31	-

(-) = Not detected.

The TICs observed for each test condition are given in Table A-12. Concentrations for the TICs are semiquantitative. Identification of these compounds is based on comparisons to library reference mass spectra and manual inspection. Concentrations of the TICs are based on the responses relative to the internal standards. More accurate quantitation for the TICs is possible only by conducting analysis of authentic standards.

3. FTIR

Tables A-13 and A-14 summarize FTIR results and toxicity data for each compound. Table A-13 is divided by fire phase and Table A-14 shows the highest 1-minute reading, equivalent worst-case concentration, and emission rate. Figures A-10 through A-12 show the data in graphical form. Detailed results are given in Appendix C. Note that carbonyl fluoride was not yet identified, and its concentration was not known at the time of the Screening Study. The concentration variations seen in the figures are caused by the firefighter attack method. Before agent application, the beam path is usually on the edge of the plume. As agent is applied, the force of the extinguisher vapor forces the plume directly into the beam path, which varies as the firefighter moves the extinguisher nozzle in a low sweeping motion.

The presence of significant concentrations of acid gases suddenly changed the FTIR from an experimental technique to the critical measurement method. The need for a confirming method sensitive to the acid gases also became apparent.

B. SAMPLE PROCEDURES

The following sections describe the sampling equipment and procedures used for the Screening Study. Sections covered include Summa[®] canisters, Tenax[®]/Carbosieve[®], PUF, and FTIR.

CO monitoring of the plume, using standard stack-type continuous emission monitors (CEMs), was also performed, but did not detect CO levels above 10 ppm, apparently due to plume dynamics. For this reason, CO monitoring by CEM was dropped for the Main Test. (The FTIR was also measuring CO in the plume.)

Note that all plume samples were split from a common probe located within the plume (Figure 1). The probe housing consisted of a 2-inch schedule 40 stainless steel pipe positioned to draw sample from a height of 25 feet centered above the middle of the fire. The probe housing protected a 5/8-inch id (inner diameter) Teflon[®] tubing through which sample was drawn. The Teflon[®] tube was withdrawn, cleaned, and recovered as sample for each test.

TABLE A-12. SVO TENTATIVELY IDENTIFIED COMPOUNDS
(TICS) OBSERVED IN RUN 6 (JP-4 ONLY)
AND RUN 5 (HALON 1211).

TICs
Methyl Naphthalene
1,1'-Biphenyl
Dimethyl Naphthalene
Ethenyl Naphthalene
Phenyl Naphthalene
Alkylated Ketones
Alkylated Alcohols

TABLE A-13. FTIR CONCENTRATIONS BY FIRE PHASE
[ppm (v/v)].

Compound (IDLH)	Test No.: Agent:	3 None	4 H1211	5 H1211
Acetylene (none)	Fuel only	0	0	0
	Fire	1.2	2.5	2.6
	Agent		0.2	0
	Out			
Agent (5,000) ^a	Fuel only		0	0
	Fire		0	0
	Agent		840	516
	Out		176	15
HCl (100)	Fuel only		0	0
	Fire		0	0
	Agent		39	41
	Out		1	0
HBR (50)	Fuel only		0	0
	Fire		0	0
	Agent		44	51
	Out		1	0
HF (30)	Fuel only		0	0
	Fire		0	0
	Agent		18	15
	Out		1	0
COF ₂ (15) ^b	Fuel only		0	0
	Fire		0	0
	Agent		8.7	15
	Out		0.3	0
JP-4 (5,000)	Fuel only	0	0	106
	Fire	37	15	22
	Agent		51	33
	Out		29	35
CO (1,500)	Fuel only	0	0	0
	Fire	57	3	0
	Agent		86	132
	Out		41	0

^a Typical value for most halocarbons.

^b Estimate from equivalent HF formation.

TABLE A-14. FTIR SUMMARY OF EMISSIONS.

Compound (IDLH)	Test No.: Agent:	3 None	4 H1211	5 H1211
Acetylene (none)	1-min max (ppm)	2.8	2.8	3.4
	Avg. conc. worst case (ppm)	1.2	2.6	2.6
	Emission g/kg agent		0.4	0.8
Agent (5,000) ^a	1-min max (ppm)		1,440	640
	Avg. conc. worst case (ppm)		990	540
	Emission g/kg agent		1,000	1,000
HCl (100)	1-min max (ppm)		42	54
	Avg. conc. worst case (ppm)		38	41
	Emission g/kg agent		18	17
HBR (50)	1-min max (ppm)		49	76
	Avg. conc. worst case (ppm)		43	51
	Emission g/kg agent		21	46
HF (30)	1-min max (ppm)		20	19
	Avg. conc. worst case (ppm)		18	15
	Emission g/kg agent		2.2	3
COF ₂ (15) ^b	1-min max (ppm)		9.4	21
	Avg. conc. worst case (ppm)		8.6	15
	Emission g/kg agent		3.5	11
JP-4 (5,000)	1-min max (ppm)	75	75	64
	Avg. conc. worst case (ppm)	37	83	129
	Emission g/kg agent		79	225
CO (1,500)	1-min max (ppm)	172	122	183
	Avg. conc. worst case (ppm)	57	127	132
	Emission g/kg agent		22	41

^a Typical value for most halocarbons.^b Estimate from equivalent HF formation.

FTIR DATA

Test #3

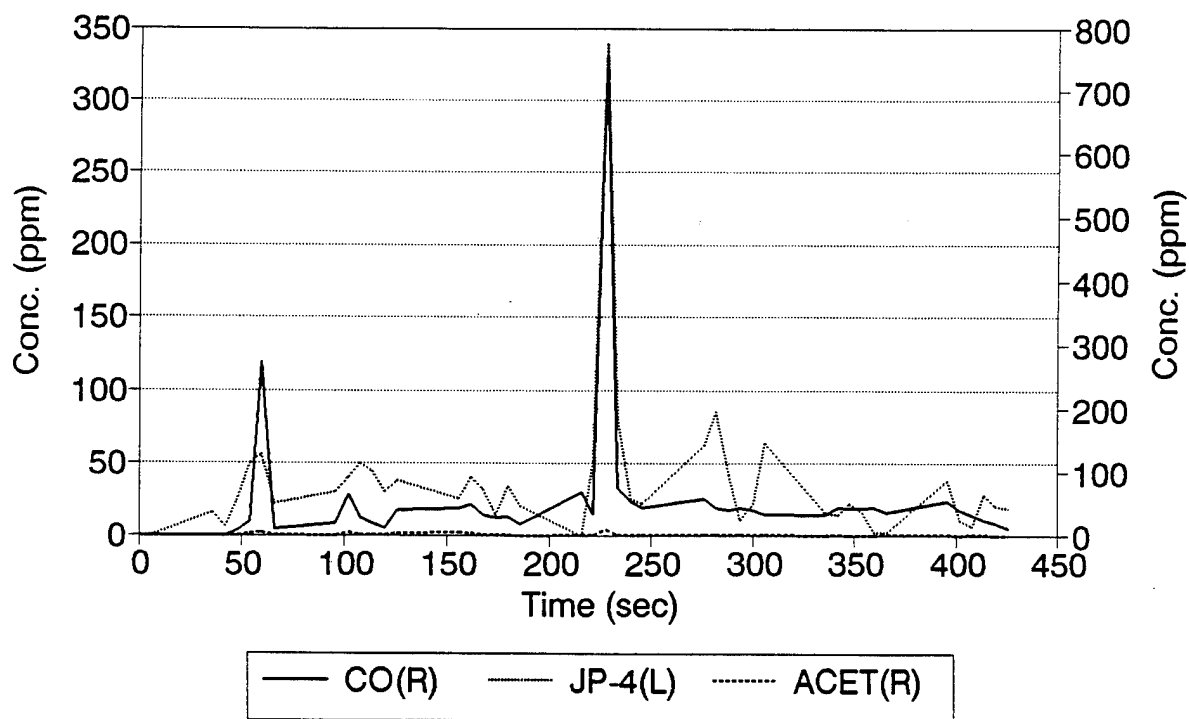


Figure A-10. Run 3 FTIR data.

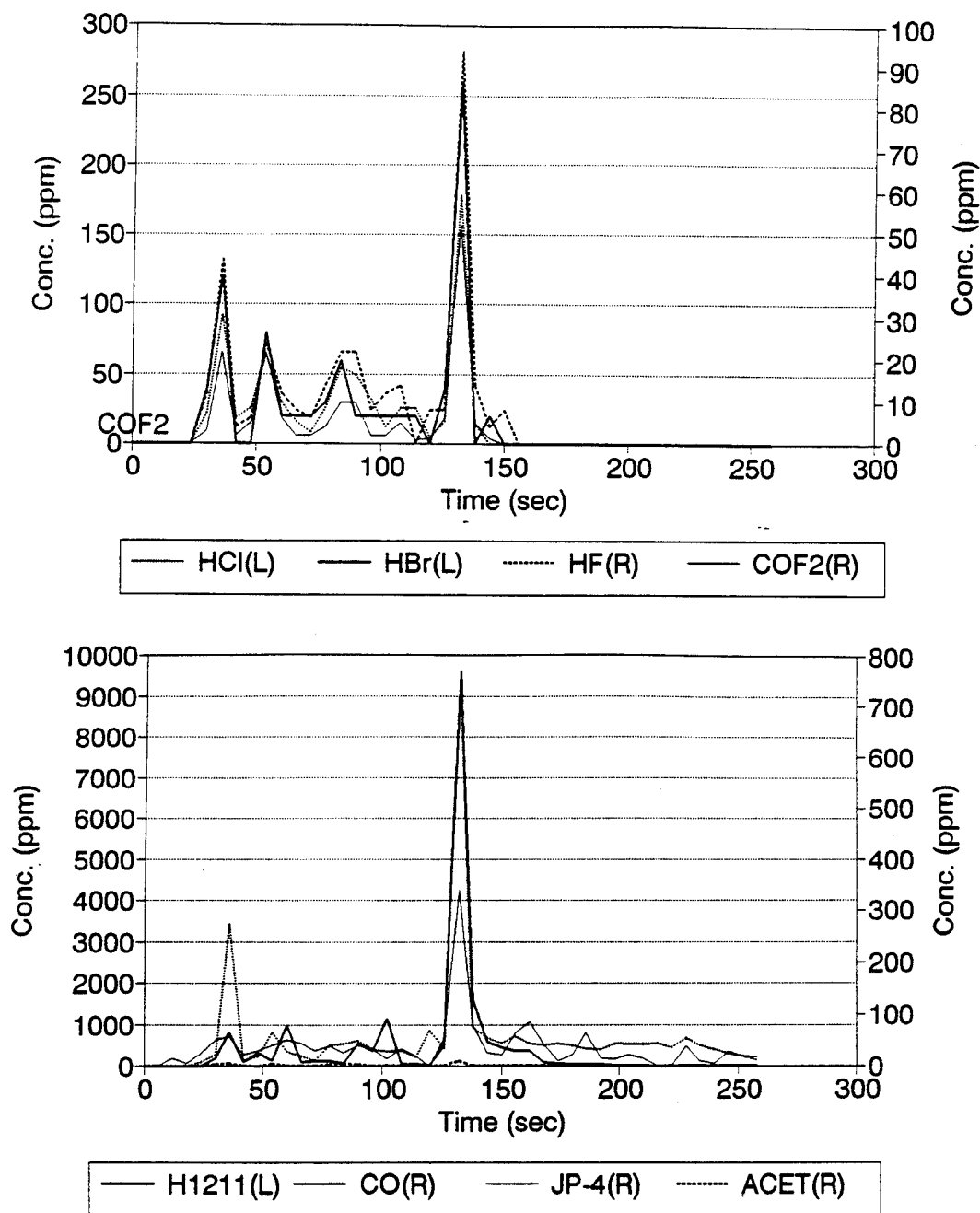


Figure A-11. Run 4 FTIR data.

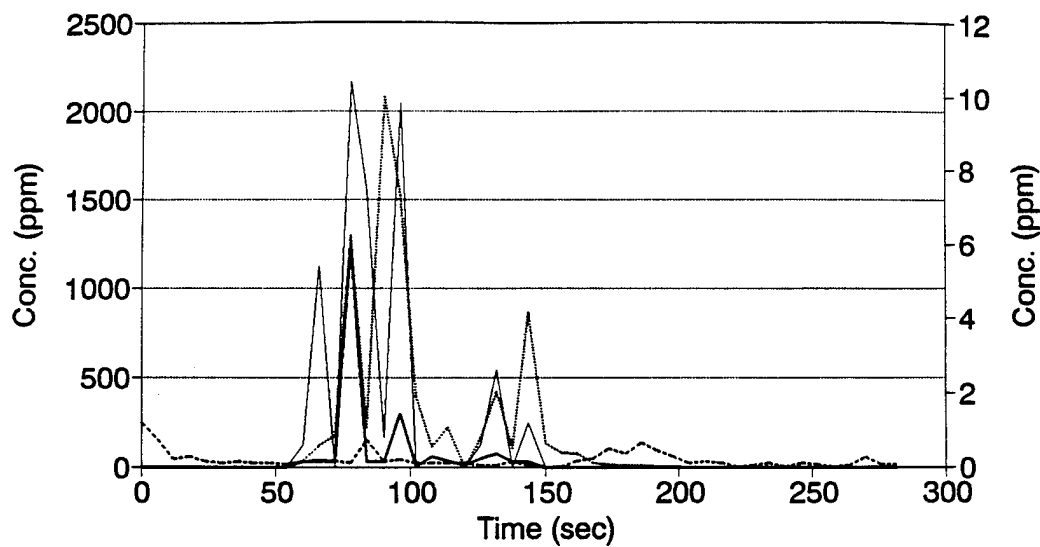
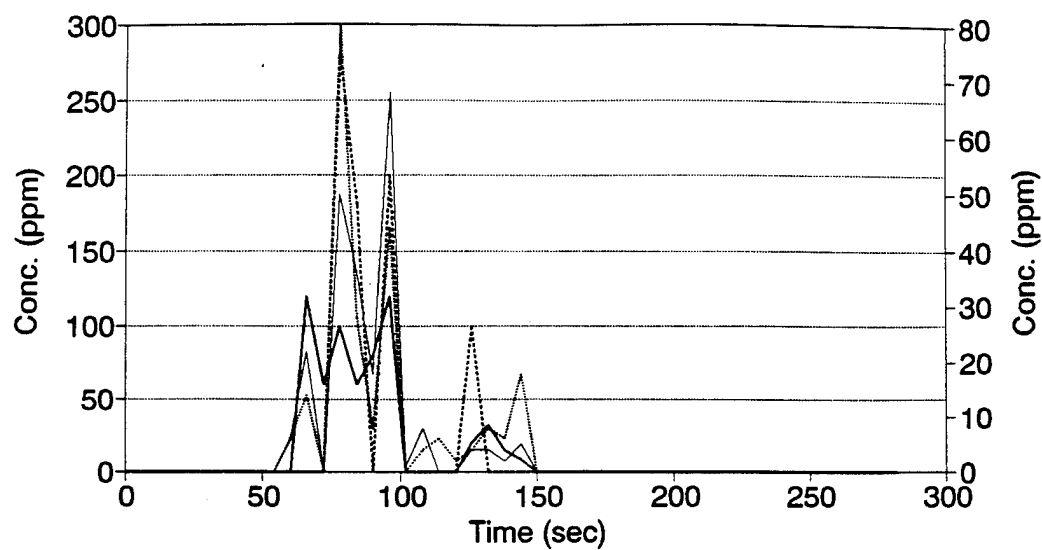


Figure A-12. Run 5 FTIR data.

The lower end of the plume sampling probe was connected to the plume sampling manifold. This manifold provided sample splits to the PUF, Summa®, Tenax®/Carbosieve®, and CO samplers. The PUF sampler pump provided the suction for drawing sample through the manifold, with branching tap lines for the Summa®, Tenax®/Carbosieve®, and CO monitor. The manifold itself was made from a section of stainless steel pipe fitted with 1/4-inch Swagelok connectors for attaching the various sampling tubes. The manifold fit directly onto the PUF sample intake, just upstream of the PUF particulate filter.

1. Summa® Canisters

Summa® canisters were set up to sample both the plume and firefighter locations. One upwind (background) sample was also collected. Plume samples were collected using the plume sampling manifold, while firefighter location samples were drawn directly into the appropriate canister. In the latter case, canisters were set up on stands to provide a sample intake height of about 4.5 feet at all locations.

Sample collection involved opening the main valve fully to draw sample through the glass capillary at critical velocity. Sample collection then proceeded for a total of roughly 6 to 8 minutes—concurrent with the other sampling methods. Thus, sampling continued for several minutes after the fire was out to allow adequate collection of fumes, smoke, and so forth.

Following collection of the sample, the Summa® cans were sealed by closing the main valve and removing the glass capillary. The vacuum level within the canister was measured and recorded on the field data sheet. Each canister was then attached to a dry nitrogen line and filled with dry nitrogen pressurized to 32 to 36 mm Hg. The pressurized canisters provided a stable environment for shipping samples back to the laboratory for analysis and allowed for quick identification of invalid samples caused by leaks. An ID tag was attached to each canister with the serial number, sample number, location, and date. Figure A-13 shows a typical data log sheet.

2. Tenax®/Carbosieve® Samplers

The Tenax®/Carbosieve® sampler consisted of two adsorbent resin traps (one Tenax®, one Carbosieve®), a sampling pump, a calibrated dry gas meter, and a rotameter. The Tenax® trap contained approximately 1.6 grams of Tenax®. The Carbosieve® cartridge contained approximately 2.0 grams of carbon molecular sieve (CMS). Each cartridge was embossed with a unique sample number at one end of the glass tube. A known volume of air was collected from the plume manifold air stream and drawn through the cartridge at a known flow rate of approximately 1.0 L/min. Samples at the firefighter locations were drawn directly into the resin trap. The maximum air volume collected was 10 liters. The sample collection method was

CANISTER SAMPLING FIELD DATA SHEET

A. GENERAL INFORMATION

Site Location: _____

Shipping Date: _____

Site Address: _____

Canister Serial No.: _____

Sampler ID: _____

Operator: _____

Sampling Date: _____

Canister Leak _____

Check Date: _____

B. SAMPLING INFORMATION

Temperature

	Interior	Ambient	Maximum	Minimum
Start				
Stop				

In Press.	
Fin. Press.	
Fin. Dilution Press.	
Ambient Press.	

Sampling Times

	Local Time	Elapsed Time Meter Reading
Start		
Stop		

Flow Rates

Canister Flow Rate	Flow Controller Readout

Orifice Size: _____ Orifice Type: _____

Sampling System Certification Date: _____

Quarterly Recertification Date: _____

Signature

Figure A-13. Canister Sampling Field Data Sheet.

based on procedures described in USEPA's *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air*, Method TO2, with modifications. Figure A-14 shows a typical data log sheet.

a. Preparation of the Adsorbent Resin Traps

The adsorbent cartridges were 10-cm glass tubes with an external diameter of 1.6 cm. The glass tubes were hand packed with Tenax[®] resin or Carbosieve[®] S-III (Supelco, Inc.). The packing was held in place by Teflon[®]-coated stainless steel screens and clips at each end of the resin layer. The traps were thermally conditioned by flowing organic-free nitrogen (50 to 100 mL/min) through the cartridge while heating it to 175°C for at least 16 hours.

During the thermal conditioning, the cartridges were installed in a specially designed heated manifold that permitted the nitrogen purge from the traps to be individually monitored by a GC equipped with a flame ionization detector (FID). The conditioning was continued until the FID response indicated the traps were clean (less than 5 ppb total hydrocarbon as propane). All trap preparation was performed at MRI.

After conditioning, the cartridges were sealed with viton O-rings and stainless steel endcaps. They were placed into a precleaned metal can containing a small amount of granulated activated charcoal. The can was then sealed with a metal friction top. Cartridges were stored in the metal can at all times except when in use.

b. Tenax[®]/Carbosieve[®] Sampler Calibration

All Tenax[®]/Carbosieve[®] samplers were calibrated, checked for proper operation, and cleaned for use prior to arrival on-site. The metering system for the sampler consisted of a vacuum gauge, needle valve, a leak-free pump, a rotameter for monitoring gas flow, and a dry gas meter (low volume) with 2 percent accuracy at the required sampling rate. The rotameter and dry gas meter were checked against a volumetric bubblemeter before and after the test.

All sample transfer lines used with the Tenax[®]/Carbosieve[®] sampler, up to and including the resin cartridge, were Teflon[®] or glass with connecting fittings that were capable of forming leak-free vacuum-tight connections without the use of sealing grease.

c. Collection of Tenax[®]/Carbosieve[®] Sample

The sampling flow rate of the Tenax[®]/Carbosieve[®] sampler was set to approximately 1.0 L/min using a rotameter that had been checked against a volumetric bubblemeter. "Dummy" cartridges were placed in line during flow-rate determinations. The rotameter was included in the sampling system to allow periodic observation of the flow rate without disrupting the sampling process.

MIDWEST RESEARCH INSTITUTE VOST										
Run No. _____					Operator _____					
Project No. _____					Sample Location _____					
Date _____					VOST Unit I.D. _____					
Plant _____					VOST Console Unit _____					
Barometric Pressure _____					Meter Correction _____					
Site to Baro. Elevation (ft) _____					Probe Lk Ck: Initial P / F Final P / F					
Corrected B.P. (0.1 in/100 ft) _____					Console Lk Ck: Initial P / F Final P / F					
Rotometer Setting _____										

Clock Time (24 hr)	Dry Gas Meter Reading (L)	Meter Temp. °C	Probe Temp. °C	Vacuum Pressure in. Hg	Tenax Temp. °C	Tenax		Carbosieve		Train Leak Check
						Tube No.	Sample No.	Tube No.	Sample No.	

Comments: _____

	Tenax		Carbosieve	
	Tube No.	Sample No.	Tube No.	Sample No.
Blank Tube I.D.				
Field BI				
Trip BI				

91-39 SEV date from 2 071191

Figure A-14. Adsorbent Cartridge Sample Data Form.

Just prior to initiation of the sample collection process, the Tenax® and Carbosieve® cartridges were removed from their sealed containers. The Tenax® cartridge was installed first, with the exit (unmarked) end of the tube connected to the inlet of the Carbosieve® trap. The exit (unmarked) end of the Carbosieve® tube (black) was connected to the inlet of the sampling apparatus. The endcap was left on the sample inlet, and the entire system was checked by activating the sampling pump and observing that no flow was obtained over a 1-minute period. The pump was then shut off.

The following parameters were recorded on the field sampling data form: sample number (embossed on each of the cartridges); date; sampling location; run number; ambient temperature; barometric pressure; dry gas meter reading; and the serial numbers of the pump, gas dry meter, and rotameter.

Immediately prior to ignition of the fire, the endcap on the inlet of the sampler was removed, and the pump was started. The start time and the initial flow rate were recorded on the sampling data form. The sample was collected (for about 6 to 8 minutes during the extinguishment of the fire and for a period after the fire was out). At the end of the sampling period, the final flow rate was recorded, the pump was turned off, and the clock time was recorded.

The cartridges were removed (one at a time), and the end caps were replaced. The sealed cartridge were placed into a precleaned metal can containing a small amount of granular activated charcoal and sealed with a friction metal top. The metal can was placed on ice until it was ready for packaging and shipment to MRI.

The total volume sampled (V_s) at standard conditions, 760 mm Hg and 25°C, was calculated from the following equation:

$$V_s = V_m \times \frac{P_a}{760} \times \frac{298}{273 + T_a}$$

where

P_a = average barometric pressure, mm Hg

T_a = average ambient temperature, °C

3. PUF Samplers

As with the other stationary methods, PUF samplers were set up to sample both the plume and firefighter locations. One upwind (background) sample was also collected. Plume samples were collected using the plume-sampling manifold, while the other samples were drawn directly into the appropriate sampler. Samplers were positioned on-site as determined to give the most representative samples. Figure A-15 shows a typical data log sheet.

EPA Method TO4 was followed in installing the PUF sample cartridges. Latex or cotton gloves were used to prevent contamination of the cartridge. Following insertion of the cartridge, the power was turned on, and the test run began. Sample was collected for the next 6 to 8 minutes.

Before departure for the field, staff weighed and placed PUF particulate filters in individually marked petri dishes. Petri dishes were cleaned with distilled deionized water and methanol before use.

Following sampling activities, staff rinsed the plume sampling probe with methanol and brushed to remove particulate. The probe rinse was collected in an amber bottle and sealed for return to the laboratory.

4. FTIR

The source-spectrometer line-of-sight was positioned 4 feet high, just outside the fire ring (within 1 meter) on the downwind south side, perpendicular to the line of firefighter approach and approximately perpendicular to the wind. The source was positioned on the west side, and the spectrometer on the east side of the pit (see Figure A-16). During Test 1, both source and spectrometer were positioned just outside the inner wind screens 50 feet (15 meters) from the pit. During later tests, the spectrometer was moved back to 58 feet (17.5 meters) from the pit.

The fire pit was 3 meters wide, and we assumed a 5-meter average plume width along the FTIR beam path after allowing for plume expansion. This effective beam path was used instead of the 36-meter total beam path because most of the total path was in clear air.

During Tests 1 and 2, the FTIR was operated with a repeating series of 3 scans at 0.5 cm^{-1} , followed by 3 at 4 cm^{-1} , 3 at 32 cm^{-1} , 3 at 4 cm^{-1} , and finally 3 at 0.5 cm^{-1} . This was done as a result of preliminary tests with a test fire in June that indicated the spectrometer was adversely affected by rapid flame changes during the scan period. Lower resolution scans shorten the scan period and, therefore, ensure useable data regardless of rapid fluctuations in the fire. After examining the first day's data, none of the 0.5 cm^{-1} scans were flawed, and the lower resolution scans showed inadequate fine structure for identification of the complex mixtures present in the smoke plume. Only the 0.5 cm^{-1} scans from Test 3 were processed. Starting with Test 4, all data were collected as a series of single 0.5 cm^{-1} scans obtained about every 6 seconds.

C. ANALYSIS PROCEDURES

The analytical methods used for the Air Force Screening Study were specifically chosen based on the investigative nature of the testing. The primary objectives were to identify the chemical species released during firefighting exercises and to evaluate

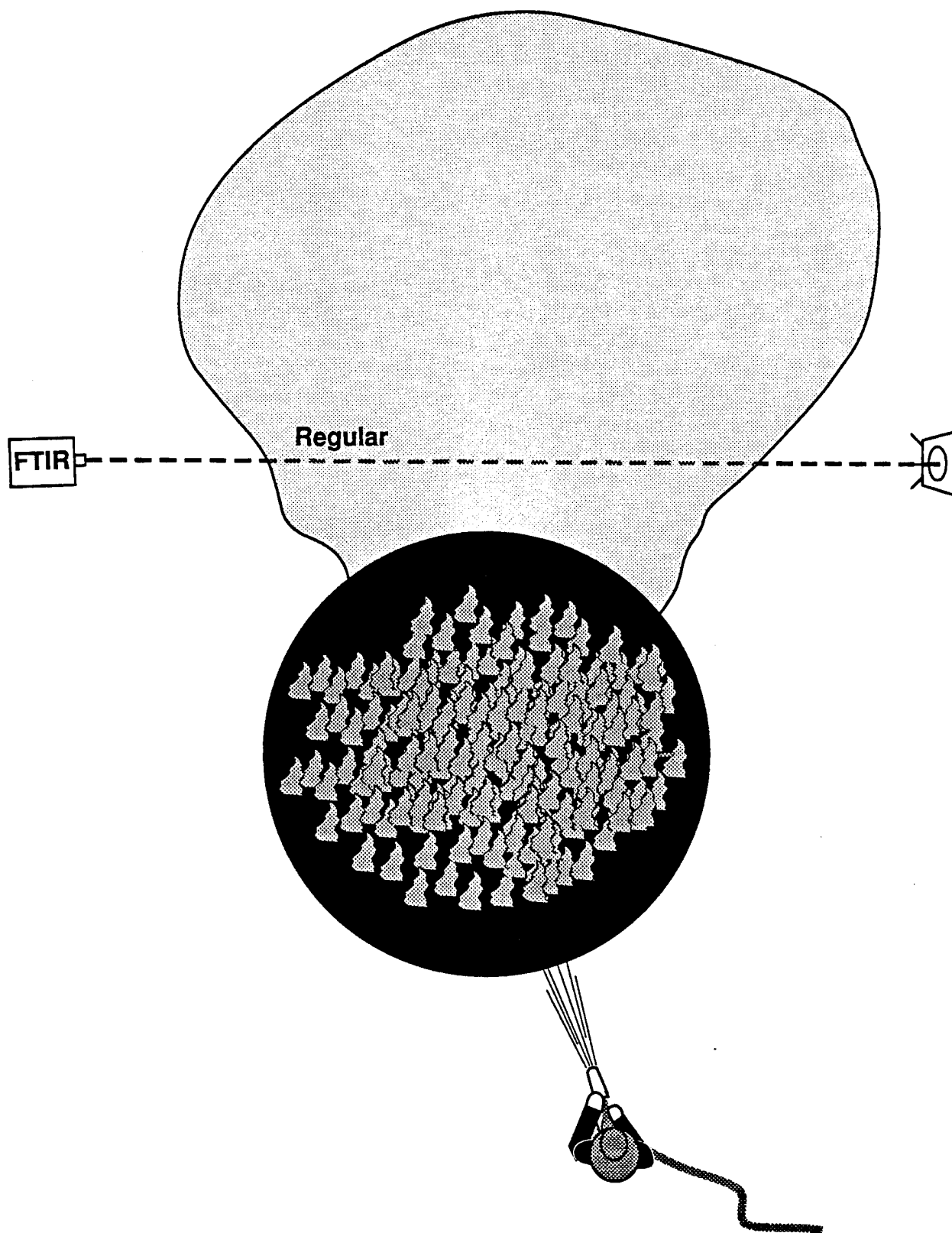


Figure A-16. FTIR beam position.

analytical methodologies for the Main Test. Therefore, the analytical methods were intentionally less rigorous than for the Main Test, with only the minimum acceptable level of quality assurance. The analytical methods were, however, based on several well-established EPA methods and met the analytical requirements for the Screening Study.

1. Summa® Canisters

The analysis of samples collected by the Summa® canisters for the Screening Study was based on several methods, including EPA Methods TO14, 5040, and 8260. In brief, the contents of the Summa® canister were transferred to a Tenax® adsorbent tube (referred to as a VOST trap), where a surrogate and internal standard were added. The VOST trap was then thermally desorbed onto an "analytical" trap, which also consisted of an adsorbent material, and the VOCs were further concentrated. The "analytical" trap was then thermally desorbed directly onto a GC/MS system for chromatographic separation and mass measurement.

Before sample analysis, the analytical system was calibrated for proper performance with various instrumental checks, including mass calibration, proper mass tuning, three-point calibration curve, and system blank. All of these checks were performed daily except for the three-point calibration curve, which was run initially to determine the response of each target analyte covering a predetermined concentration range. The limited number of analytes chosen for the Screening Study were based on the likelihood of their presence during the research test. This procedure also allows for the identification of "unknown" or TICs.

2. Tenax®/Carbosieve® Traps

Samples collected on Tenax®/Carbosieve® traps, filled with either Tenax® or Carbosieve® adsorbents, were analyzed by GC/MS procedures based on EPA Methods TO2, 5040, and 8260. Most of these analytical approaches are identical to the Summa® method. Briefly, the samples collected on Tenax®/Carbosieve® traps were initially spiked with surrogates and internal standards. The contents of the traps were thermally desorbed onto an "analytical" trap, which was then thermally desorbed directly onto a GC/MS system for chromatographic separation followed by mass measurement. The target analytes for the Tenax®/Carbosieve® trap analysis were identical to those of the Summa® method.

3. PUF Cartridges

Nonvolatile, or extractable, organics collected on PUF cartridges and particulate filters were measured by an analytical method based on EPA Methods TO4 and 8270. The organics were extracted from the PUF cartridges and particulate filters by Soxhlet extraction with an organic solvent and concentrated to a final liquid extract. Recovery surrogates were added to the analytical system to measure the overall

efficiency of the extraction method. A portion of the final sample extract was then injected onto a GC/MS system for chromatographic separation, and mass measurements were performed. The method can help identify compounds of potential concern and provide quantitative measurement of preselected target analytes.

Quality checks provided by this method include extraction efficiency, instrumental calibration, tuning, and a three-point calibration curve for the target analytes.

4. FTIR

The data were initially stored as interferograms and converted to single beam data immediately after each test. A 100-scan averaged background scan was collected after the end of each test and used as the reference to convert the single beam data to absorbance units for quantitative analysis. Several regions with strong water and carbon dioxide interferences were blanked out, and the resulting spectra were manually compared with the target list to identify the various components. Carbon monoxide, Halon 1211, hydrocarbons, hydrogen chloride, hydrogen bromide, and hydrogen fluoride accounted for all but two features that stood clearly above the background noise. A search of the Hanst quantitative library identified a sharp peak at 729.6 cm^{-1} as acetylene, and some of the stronger absorbing spectra showed enough of the smaller side peaks to provide a good match for this peak.

The remaining unknown was a single sharp peak at 774.1 cm^{-1} with absorbances as high as 0.5 in some scans. It was not methyl fluoride or PFIB. The narrowness of the peak indicated that the molecule must be small. Peak shape was identical with the 729.6 cm^{-1} acetylene peak. This peak was finally identified following the Main Test as carbonyl fluoride.

Figure A-17 shows an annotated spectrum from the maximum intensity scan (No. 23) for Test 4. Several spectral regions show saturated detector signal, such as the Halon 1211 bands at 900 and 1100 wavenumbers and most of the water and carbon dioxide interference bands. The Halon 1211 band at 500 wavenumbers is too noisy for good quantitation. The sharp acetylene band at 729 wavenumbers is usually the only measurable feature for this compound. The sharp 774 wavenumber band for carbonyl fluoride is the best location for this compound up to about 100 ppm-m where nonlinearity can begin. For high concentrations of Halon 1211, the weak band at 980 wavenumbers is best. Those at 900 and 100 are best at less than 1 absorbance unit. From about 1200 to 2000, sharp water bands begin to interfere, although useful gaps do exist throughout most of the region.

At 1900 wavenumbers, the broad doublet secondary carbonyl band that was used at concentrations above 60 ppm-m appears. The complex carbon monoxide band is between 2050 and 2250, part of which is superimposed on weak Halon 1211 bands. The carbon dioxide bands at about 2350 are badly saturated. The series of

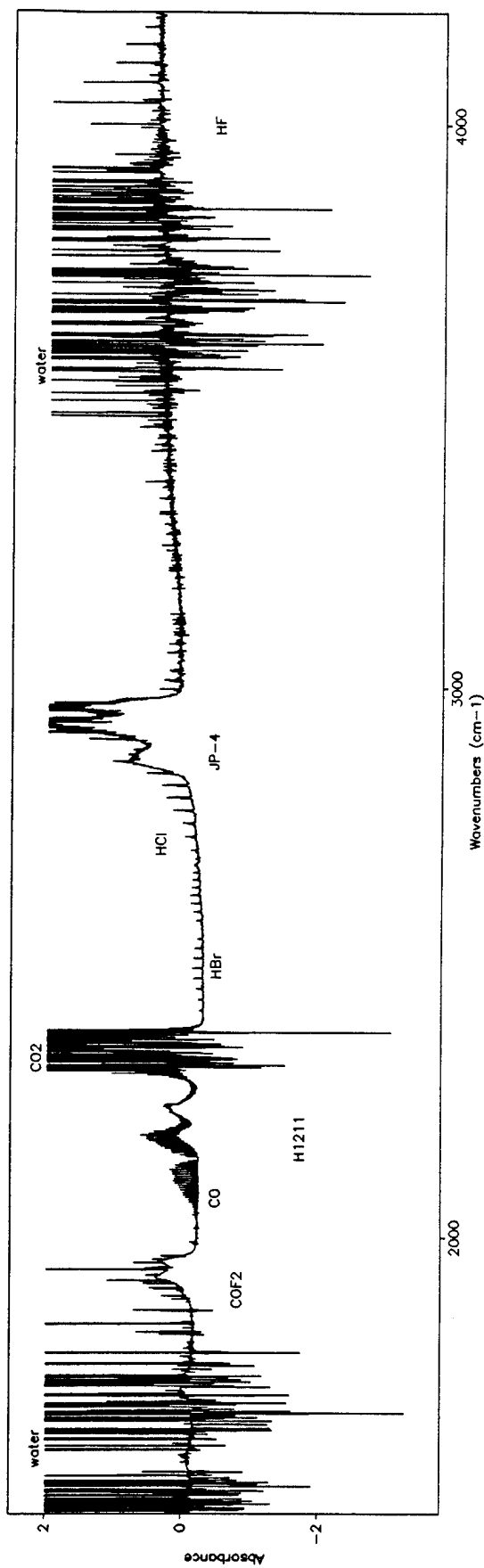
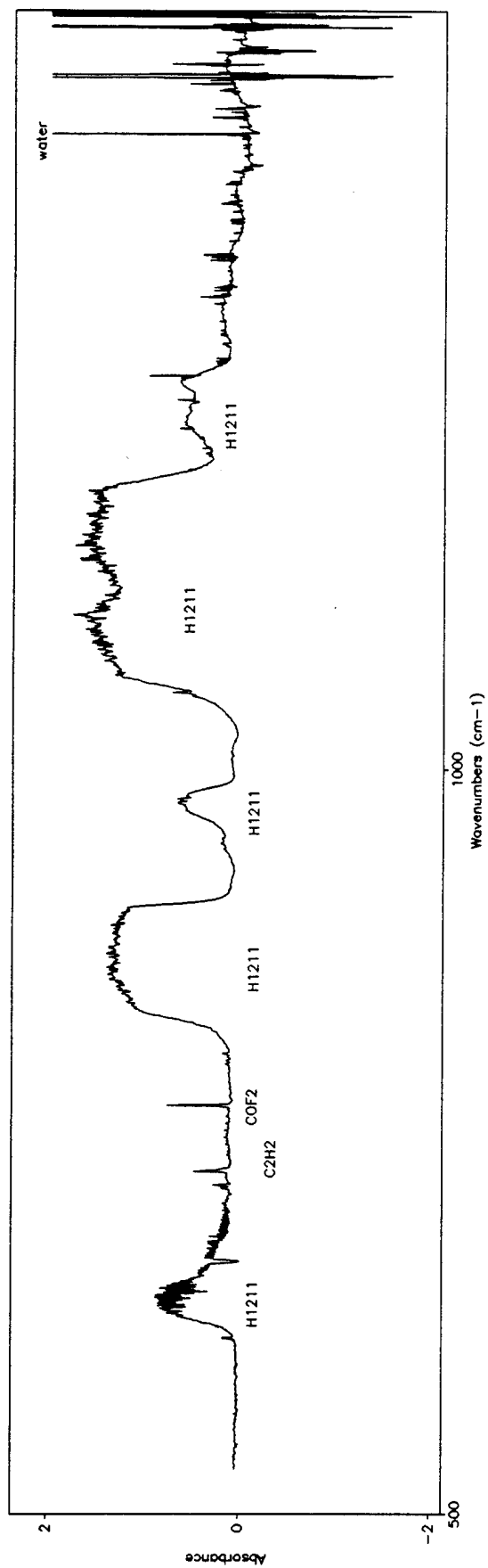


Figure A-17. Maximum Intensity Spectrum from Run No. 4.

sharp HBr bands begins just above 2400, and the characteristic doublet HCl bands extend from about 2700 to 3100. The broad double JP-4 peak at 2850 to 3000 is superimposed on some of the HCl bands, and noise spikes from detector saturation obscure portions of the JP-4 bands. More water spikes begin at about 3000 and continue until 4000 wavenumbers. The lower half of the HF reference peaks are lost to water interferences, but the higher section that runs from about 4000 to 4200 is visible as sharp single spikes.

Compound quantitations were performed with every useable peak for each compound. Usually the median of all the peak quantitations was used. Hexane was initially used as the reference compound for JP-4, and only the broad 2900 region peak complex was useable. For acetylene, usually only the 729.6 peak was strong enough to use. The averages of the 900 and 1100 peaks were used for Halon 1211, except when the absorbance was high enough to show saturation, in which case the 980 peak was used. The data for CO were recalculated after the Main Test was completed. A shortened list of peaks was used when several portions of the original set were found to be subject to H₂O interferences. JP-4 was recalculated using an actual JP-4 reference spectrum, and carbonyl fluoride was processed after obtaining a reference spectrum.

Reported values that did not show the correct peak maxima were rejected. Any readings below the equivalent of a 0.01 absorbance primary peak were also rejected as indistinguishable from noise that varied between 0.01 and 0.03 absorbance, and spectra showing low multiples of the detection limit were visually inspected and rejected when the normal peak pattern was absent. Table A-15 shows the approximate detection limit equal to the normal peak noise signal observed.

TABLE A-15. FTIR DETECTION LIMITS.

Compound	Detection limit	
	(ppm-m)	(ppm)
Halon 1211	20	4
CO	20	4
Acetylene	1	0.2
JP-4	10	2
HCl	20	4
HBr	100	20
HF	5	1

APPENDIX B

SAMPLE CALCULATIONS

This section contains example calculations of those used in sampling, analysis, and modeling activities for the study. Sample calculations are divided into the following subsections.

- A. Tenax[®]/Carbosieve[®] and Tenax[®]/charcoal—Sample volume and sample concentration calculations.
- B. Summa[®] Canisters—Sample volume and sample concentration calculations.
- C. PUF—Sample volume, semivolatile and PCDD/PCDF sample concentrations.
- D. FTIR—Peak area, instantaneous peak heights, and 1-minute rolling averages are calculated.
- E. Vertical Profile—Sample volume and sample concentration calculations.
- F. Draeger Tubes—Equivalent concentrations for HF, HCl and COF₂
- G. Modeling—Emission rates, concentrations at a distance, IDLH values and PEL levels.
- H. Community Exposure—8-hour and 24-hour concentrations.

A. TENAX[®]/CARBOSIEVE[®] AND TENAX[®]/CHARCOAL

1. T/C Volume Calculations

Sample 1035, Main Test, Run 1 used as an example.

Field data: Ambient temperature = 70°F (21.1°C)

BP = 24.870 in Hg (632 mm Hg)

Dry gas meter reading = 0.989 ft³

Y factor for DGM #1342 = 0.9520

Convert ft³ to L volume

$$0.989 \times 28.32 \text{ L/ft}^3 = 28.01 \text{ L of sample gas}$$

$$\text{Correct to STP using } Y * \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$0.9520 * \left(\frac{24.870 * 28.01}{21.1 + 273} \right) = \left(\frac{29.92 * V_2}{298} \right)$$

$$V_2 = 22.46 \text{ L sample gas at STP.}$$

Sample Nos. 3037, 5037, 6037 have no volume measurements. These samples were collected as field blanks.

2. T/C Concentration Calculations

Sample No.: 5033
 Date Analyzed: 31 Oct 91
 GC/MS filename: 6207J31T5
 Analyte: Benzene

Step 1: Determine the amount of analyte detected.

- a. Determine the average relative response factor (RRF) for each analyte from the standard calibration curve.

$$RRF = \left(\frac{\text{Std. area}}{\text{Std. amt.}} \right) \left(\frac{\text{Ref. amt.}}{\text{Ref. area}} \right)$$

$$= \left(\frac{12,788}{10} \right) \left(\frac{50}{293,067} \right)$$

$$RRF = 0.218$$

	File			
	J29TQ14	J29TQ15	J29TQ16	K04TQ4
Ref. amt.	50	50	50	50
Ref. area	293,067	281,490	302,712	195,655
Std. amt.	10	50	250	1,250
Std. area	12,788	49,669	267,409	816,165
RRF	0.218	0.176	0.177	0.167

$$\text{Average RRF} = \frac{0.218 + 0.176 + 0.177 + 0.167}{4}$$

$$= 0.185$$

b. Amount detected

$$= \frac{[(\text{area}) * (\text{ref. amt.})]}{[(\text{ref. area}) * (\text{RRF})]}$$

$$= \frac{(90,758) (50 \text{ ng})}{(334,807) (0.185)}$$

$$\text{Amt. detected} = 73.264 \text{ ng}$$

Step 2: Determine the concentration of the analyte (expressed as ng/L) using the corrected (STP) volume sampled and the amount of the analyte detected.

a. Concentration (ng/L)

$$= \frac{(\text{Amt. detected})}{(\text{corrected vol. sample})}$$

$$= \frac{73.264 \text{ ng}}{6.09 \text{ L}}$$

$$\text{Conc.} = 12.030 \text{ ng/L}$$

Step 3: Convert the concentration to ppb.

a. Determine the concentration expressed as moles/L.

$$\frac{12.030 \text{ ng/L}}{78 \text{ g/mole}} = 0.154 * 10^{-9} \text{ moles/L}$$

b. Determine the concentration expressed as ppb (by volume).

$$(22.4 \text{ L/mole}) \left(\frac{298^{\circ}\text{K}}{273^{\circ}\text{K}} \right) = 24.5 \text{ L/mole @ } 760 \text{ mm Hg and } 298^{\circ}\text{K}$$

$$(0.154 * 10^{-9} \text{ moles/L}) (24.5 \text{ L/mole}) = 3.773 * 10^{-9} \text{ L/L}$$

$$(3.773 * 10^{-9} \text{ L/L}) (10^9) = 3.773 \text{ ppb}$$

B. Summa® CANISTERS

1. Sample Volume Calculation

Sample 1012, Main Test, Run 1 used as example.

Field data: Ambient temperature = 70°F (21.1°C)

BP = 24.870 in Hg (632 mm Hg)

Canister volume = 6.0 L

Initial (evacuated) pressure = -61.5 cm Hg

Final (sample) pressure = -36.4 cm Hg

Final (dilution) pressure = 20.0 cm Hg

There are three separate components in each Summa® canister.

1. Initial volume after evacuation.
2. Volume of sample itself.
3. Volume of dry N₂ used for dilution.

Step 1: Initial volume after evacuation—using the ideal gas law where $PV = nRT$

$$\frac{(632 + [-615]) \text{ mm Hg}}{760 \text{ mm Hg}} * 6.0 \text{ L} = n (.0821) \frac{\text{L-atm}}{\text{K-mol}} (21.1 + 273) ^\circ\text{K}$$

$$n = 0.0056 \text{ moles}$$

Step 2: Volume of sample gas—again, using $PV = nRT$

$$\frac{(632 + [-364])}{760} * 6.0 = n (.0821)(21.1 + 273)$$

$$n = 0.0876 \text{ moles}$$

$$.0876 - .0056 = .0821 \text{ moles of sample gas}$$

$$(.0821 \text{ moles}) * .0821 * 298 = 2.008 \text{ L sample at STP.}$$

Step 3: Volume of dry N₂ dilution— $PV = nRT$

$$\frac{(200 + 632)}{760} * 6.0 = n (.0821)(21.1 + 273)$$

$$n = 0.2720 \text{ moles gas}$$

$$(0.2720 - .0876) = 0.1844 \text{ moles of dilution gas}$$

$$(0.1844 \text{ moles}) * .0821 * 298 = 4.512 \text{ L of N}_2 \text{ at STP}$$

2. Sample Concentration Calculations

Field conditions:

Sample No.: 6013, Main Test
Date: 18 Oct 91
Time: 8:30 a.m.
Barometric pressure: 24.935 in Hg (633.3 mm Hg)
Temperature: 65°F (18°C)
Sample type: Firefighters

Laboratory conditions:

Analysis date: 19 Nov 91
Temperature: °C (298°K)
GC/MS filename: K19T2
Analyte: Benzene

Using calculations similar to those in Part 1, above,

Volume of sample = 2.310

Volume of dilution = 4.200

Total volume = 6.510

Step 1: Determine the dilution factor (DF)

$$\begin{aligned} DF &= \frac{(\text{total volume})}{(\text{volume of sample})} \\ &= \frac{6.510}{2.310} \end{aligned}$$

Step 2: Determine the corrected volume of gas analyzed (corrected to 760 mm Hg and 298°K)

a. From the laboratory notebook, determine the canister absolute pressure before and after removal of the analysis volume.

b. Corrected volume analyzed

$$\begin{aligned} &= \left[\frac{(\Delta \text{ press.})}{(760 \text{ mm Hg})} \right] * \left[\frac{(298^\circ\text{K})}{(\text{lab temp. } ^\circ\text{K})} \right] * [6 \text{ L}] \\ &= \left[\frac{(128 \text{ mm Hg})}{(760 \text{ mm Hg})} \right] * \left[\frac{(298^\circ\text{K})}{(298^\circ\text{K})} \right] * [6 \text{ L}] \\ &= 1.011 \text{ L} \end{aligned}$$

Step 3: Determine the amount of analyte detected.

- a. Determine the relative response factor for each analyte from the calibration curve (as in Part A., Tenax®/Carbosieve® and Tenax®/Charcoal).

- b. Amount detected

$$\begin{aligned} &= \frac{[(\text{area}) (\text{ref amt.})]}{[(\text{ref. area}) (\text{rrf})]} \\ &= \frac{(41,386)(50,000 \text{ ng})}{(194561)(0.191)} \\ &= 55.684 \text{ ng} \end{aligned}$$

Step 4: Determine the concentration of the analyte in the original gas sample expressed as volumetric ppb.

- a. Determine the concentration of analyte in the corrected volume analyzed expressed as ng/L.

$$\frac{55.684 \text{ ng}}{1.011 \text{ L}} = 55.078 \text{ ng/L}$$

- b. Multiply by the field dilution factor to correct for field dilution.

$$55.078 \text{ ng/L} \left(\frac{6.510}{2.310} \right) = 155.122 \text{ ng/L}$$

- c. Determine the concentration expressed as moles/L.

$$\frac{155.122 \text{ ng/L}}{78 \text{ g/mole}} = 1.9887 \times 10^{-9} \text{ moles/L}$$

- d. Determine the volumetric concentration expressed as ppb.

$$22.4 \text{ liters/mole @ 760 mm Hg and 273°K} = (22.4) \left(\frac{298°K}{273°K} \right)$$

$$= 24.5 \text{ liters/mole @ 760 mm Hg and 298°K}$$

$$(1.9887 \times 10^{-9} \text{ liters/mole}) (24.5) = 48.723 \times 10^{-9} \text{ L/L}$$

$$= 48.723 \text{ ppb}$$

C. PUF SAMPLERS

1. PUF Volume Calculations

Run 1 plume sample will be used as an example.

From raw data sheet:

Run time = 13.5 min

Initial magnehelic = 10

Final magnehelic = 7

Using the calibration curve for Samplers 11605/11606 (calibration curves are identical in the magnehelic range for this study), flow rates correspond as follows:

Initial flow rate = 3.8 scfm

Final flow rate = 3.2 scfm

$$\text{Average flow rate} = \frac{3.8 + 3.2}{2} = 3.5 \text{ scfm}$$

$$\text{Sample volume} = 3.5 \text{ scfm} * 13.5 \text{ min} = 47.3 \text{ scf}$$

2. PUF Concentration Calculations

Sample No.: 1003-1005 (Run 1 plume)

Date analyzed: 22 Nov 91

GC/MS filename: K22W12

Analyte: Anthracene

PUF volume: 47.3 ft³

Step 1: Determine the amount of analyte detected.

- a. Determine the relative RRF for each analyte for each concentration in five-point calibration curve using the following equation.

$$RRF = \frac{\text{Area (T)} * \text{Conc. (IS)}}{\text{Area (IS)} * \text{Conc. (T)}}$$

where: T = Target analyte
 IS = Internal standard
 Conc = Concentration
 RRF = Relative response factor

Determine RRF using the above-named sample (1004-1005) for an example calculation.

	Cal. Std. #1	Cal. Std. #2	Cal. Std. #3	Cal. Std. #4	Cal. Std. #5
Anthracene Conc (ng/μL)	10	20	50	100	200
d ₁₀ -Phenanthrene IS Conc (ng/μL)	40	40	40	40	40
Area (T) Anthracene	10,268	26,456	57,876	112,537	199,388
Area (IS) d ₁₀ -Phenanthrene	40,836	48,028	43,387	40,596	37,915
RRF	1.006	1.102	1.067	1.109	1.052

- b. Determine the average relative response factor for each analyte from the five-point calibration curve using the following equation.

$$RRF = \frac{(RRF(\#1) + RRF(\#2) + RRF(\#3) + RRF(\#4) + RRF(\#5))}{5} = 1.067$$

Step 2: Determine the concentration of the analyte (ng/μl) using the following equation.

$$\text{Conc.}(T) = \frac{\text{Area}(T) * \text{Conc.}(IS)}{\text{Area}(IS) * \text{RRF}(T)}$$

where:

T = Target analyte
IS = Internal standard
Conc = Concentration
RRF = Average relative response factor
Conc(T) = ng/μL

Determine the concentration of the analyte detected using the following data gathered from sample No. 1003-1005.

where:

Area(T) = 87,695
Area(IS) = 52,683
Conc(IS) = 40 ng/μL
RRF = 1.067

therefore:

Conc = 62.4 ng/μL

Step 3: Determine the concentration of the analyte (μg/sample PUF) using the Dilution Factor and Split Factor in the following equation.

$$\text{Conc}(P) = \frac{\text{Conc}(T) \text{ ng/}\mu\text{l} * \text{Dilution Factor}}{\text{Split Factor}}$$

where:

T = Target analyte
IS = Internal standard
Conc(T) ng/μL = Concentration in ng/μL not including dilution factor and split factors
Conc(P) = Concentration in μg for PUF
Dilution factor = $\frac{\text{Total volume}}{\text{Original volume}}$
Split Factor = Original extracted sample portion—the archive portion
= 0.5 (50%)

therefore:

Conc(P) = 12.5 μg/PUF

Step 4: Convert the concentration to μg/m³.

a. Convert standard cubic feet (ft³) to m³ using the following convention.

$$\text{m}^3 = \text{ft}^3 * 0.02832 \text{ m}^3/\text{ft}^3$$

where: ft^3 = PUF volume calculation for plume in Run 1 (47.3 ft^3).

$$\text{Therefore } 47.3 \text{ ft}^3 * 0.2832 \text{ m}^3/\text{ft}^3 = 1.34 \text{ m}^3$$

b. Convert the concentration to $\mu\text{g}/\text{m}^3$ using the following equation.

$$\text{Conc(M)} = \frac{\text{Conc(P)}}{1.34 \text{ m}^3}$$

where: Conc(P) = Concentration of the sample extract in $\mu\text{g}/\text{PUF}$

Conc(M) = Concentration of the sample extract in $\mu\text{g}/\text{m}^3$.

$$\text{therefore: } \text{Conc(M)} = 9.32 \mu\text{g}/\text{m}^3.$$

3. PUF PCDD/PCDF Concentration Calculations

Sample No.: 2003-2005 (Run 2—Plume)

Date analyzed: 6 Dec 91

GC/MS filename: L06V24

Analyte: 2,3,7,8-TCDF

PUF volume: 41.3 ft^3

Step 1: Determine the amount of analyte detected.

a. Determine the RRF for each analyte for each concentration in a five-point calibration curve using the following equation.

$$\text{RRF} = \frac{\text{Area(T)} * \text{Conc(IS)}}{\text{Area(IS)} * \text{Conc(T)}}$$

where: T = Target analyte

IS = Internal standard

Conc = Concentration

RRF = Relative response factor

Determine RRF using the above-named sample (2003-2005) for an example calculation.

	DF-1	DF-2	DF-3	DF-4	DF-5
2,3,7,8-TCDF Conc (pg/μL)	5	10	50	250	500
¹³ C-2,3,7,8-TCDF IS Conc (pg/μL)	48	48	48	48	48
Area (T) 2,3,7,8-TCDF	959	1,944	9,532	53,359	121,209
Area(IS) ¹³ C-2,3,7,8-TCDF	9,294	9,169	9,041	9,446	10,963
RRF	0.99	1.02	1.01	1.08	1.06

- b. Determine the average RRF for each analyte from the five-point calibration curve using the following equation.

$$RRF = \frac{(RRF(\#1) + RRF(\#2) + RRF(\#3) + RRF(\#4) + RRF(\#5))}{5} = 1.032$$

Step 2: Determine the concentration of the analyte (pg/μL) using the following equation.

$$Conc(T) = \frac{Area(T) * Conc(IS)}{Area(IS) * RRF(T)}$$

where: T = Target analyte
IS = Internal standard
Conc = Concentration
RRF = Average relative response factor
Conc(T) = pg/μL

Determine the concentration of the analyte detected using the following data gathered from sample No. 1003-1005.

where: Area(T) = 2,509
Area(IS) = 13,408
Conc(IS) = 48 pg/μL
RRF = 1.032

therefore: Conc = 8.7 pg/μL

Step 3: Determine the concentration of the analyte (pg/sample PUF) using the Dilution Factor and Split Factor in the following equation.

$$\text{Conc(P)} = \text{Conc(T)} \text{ pg/}\mu\text{L} * \text{Dilution Factor} * \text{Split Factor}$$

where: T = Target analyte
 IS = Internal standard
 Conc(T) pg/ μ L = Concentration in pg/ μ l not including dilution factor and split factors
 Conc(P) = Concentration in pg for PUF
 Split Factor = Original extracted sample portion = 2
 Dilution Factor = 10 μ l (Final sample extract volume)

therefore: Conc(P) = 174 pg/PUF

Step 4: Convert the concentration to $\mu\text{g/m}^3$.

a. Convert standard cubic feet (ft^3) to m^3 using the following convention.

$$\text{m}^3 = \text{ft}^3 * 0.02832 \text{ m}^3/\text{ft}^3$$

where: ft^3 = PUF volume calculation for plume in Run 2 (41.3 ft^3).

$$\text{Therefore } 41.3 \text{ ft}^3 * 0.02832 \text{ m}^3/\text{ft}^3 = 1.17 \text{ m}^3$$

b. Convert the concentration to $\mu\text{g/m}^3$ using the following equation.

$$\text{Conc(M)} = \frac{\text{Conc(P)}}{1.17 \text{ m}^3}$$

where: Conc(P) = Concentration of the sample extract in pg/PUF
 Conc(M) = Concentration of the sample extract in pg/m^3 .

therefore: Conc(M) = 148 pg/m^3 .

D. SAMPLE CALCULATIONS—FTIR

Most of the data calculations are performed within Spectra Calc. The raw data is collected as an interferogram which Spectra Calc converts first to single-beam form by performing a Fast-Fourier Transform on the interferogram. The ratio of each sample spectrum is then compared to a reference (background) spectrum to convert to absorbance units as in

$$\text{Absorbance} = \text{Log}_{10} \left(\frac{R_y}{S_y} \right)$$

where: R_y = Single beam reading of reference spectrum at Point y
 S_y = Single beam reading of sample spectrum at Point y

The sample spectrum width is then reduced to 530 to 4,500 cm^{-1} , and readings with absorbance > 2 are clipped to that maximum value.

For concentration calculation, a library spectrum is ratioed to the sample spectrum at selected points characteristic of that compound according to either net absorbance (broad peaks) or peak area (sharp peaks).

For example, during Main Test Run 3, Scan 18, the COF_2 peak at 774 cm^{-1} was measured using the calibration file for peak area. The peak to be integrated is defined as the net area between 771.6 and 775.3 cm^{-1} . The measured area is 0.106; the response factor is .0017244 or

$$\text{ppm-m} = \frac{\text{net area}}{\text{response factor}} = \frac{.106249}{.0017244} = 61.6 \text{ ppm-meters}$$

dividing by the path length (long path = 7.4 m) gives

$$\frac{61.6}{7.4} = 8.3 \text{ ppm}$$

carbonyl fluoride
 771.6,775.3,0017244
 771.6,775.3,.0017244

Integrator Report for File G:\SC\TEST3\R2A18

Date: 7 Mar 92: Time: 14:41

Concentration of carbonyl fluoride using entire region:

Peak @ 774.067 Absorbance = .114628

Band = 771.6,775.3 Area = .106249 Conc = 61.6152

individual band values:

Peak @ 774.067 Absorbance = .114628

Band = 771.6,775.3 Area = .106249 Conc. = 61.6152

Minimum concentration = 61.6152

Maximum concentration = 61.6152

Average concentration = 61.6152

Weighted average = 61.6152

Median concentration 61.6152

For broad peaks, consider Run 4, Scan 16. Only the 1900-1950 band is useable here due to interferences. 1874 and 1984 are the baseline measurement points and each of five points are measured.

Wave No.	RF	Net absorbance	Conc ppm-m
1920.5	.0008088	.323789	400.3
1928.5	.00126415	.361044	285.6
1937.5	.00099328	.320553	322.7
1952.0	.00099688	.311639	312.6
1957.5	.00116355	.348482	299.5

The median is 312.6, divided by path (short = 5 m):

$$= \frac{312.6}{5} = 62.5 \text{ ppm}$$

carbonyl fluoride
 919,1007
 940,.0000904
 951,.00017825
 962,.00019633
 975,.00022398
 983,.000137808
 1195, 1293
 1230,.00124154
 1239,.0012472
 1243.5,.0013222
 1251,.00136444
 1256,.00152614
 1874, 1984
 1920.5,.0008088
 1928.5,.00126415
 1937.5,.00099328
 1952,.00099688
 1957.5,.00116355

Absorbance Based Quantitation Report for File G:\SC\TEST4\FF3R16

Date: 7 Mar 92; Time: 14:4

individual band values:

Average baseline for group is -.35307

Peak @ 940 Absorbance = -.0132852 Conc. = -146.961

Peak @ 951 Absorbance = -.0470295 Conc. = -263.84

Peak @ 962 Absorbance = -.0760259 Conc. = -387.235

Peak @ 975 Absorbance = -.0479064 Conc. = -213.887

Peak @ 983 Absorbance = .00630039 Conc. = 45.7186

Average baseline for group is .789687

Peak @ 1230 Absorbance = -.329819 Conc. = -265.653

Peak @ 1239 Absorbance = -.334632 Conc. = -268.307

Peak @ 1243.5 Absorbance = -.392327 Conc. = -296.723

Peak @ 1251 Absorbance = -.430755 Conc. = -315.701

Peak @ 1256 Absorbance = -.433989 Conc. = -284.37

Average baseline for group is -443301

Peak @ 1920.5 Absorbance = .323789 Conc. = 400.333

Peak @ 1928.5 Absorbance = .361044 Conc. = 285.602

Peak @ 1937.5 Absorbance = .320553 Conc. = 322.722

Peak @ 1952 Absorbance = .311639 Conc. = 312.615

Peak @ 1957.5 Absorbance = .348482 Conc. = 299499

15 useable points found

Minimum concentration = -387.235

Maximum concentration = 400.333

Average concentration = -51.746

Weighted average = -34.023

Median concentration = -213.887

Average of central 50% = -118.189

Standard deviation (central 50%) = 210.315

Additional formulas used in Tables are:

Average by phase (Scan 21 was not useable)

$$\begin{aligned}\text{Test 4 agent (HCl)} &= \frac{\sum \text{ of Scans 12-22}}{10 \text{ readings}} \\ &= \frac{228.348 + 177.43 + 54.95 + 70.75 + 205.96 + 157.07 + 45.18 + 0 + 226.77 + 8.20}{10} \\ &= 117.47 \text{ ppm}\end{aligned}$$

For highest 1-minute average, the rolling average for the past 60 seconds is calculated for each point and the highest value picked.

$$\text{Avg. conc worst case} = \frac{\sum \text{ of all readings}}{\text{No. readings during agent phase}}$$

$$\text{Mass (g/kg agent)} = \frac{\text{avg. conc worst case}}{\text{avg. conc agent}} * \frac{\text{MW compound}}{\text{MW agent}} * 1000 \text{ g/kg}$$

$$\frac{32.42}{353.08} * \frac{36.5}{155} * 1000 \text{g/kg} = 22 \text{ g/kg}$$

Run 4 HCl

$$\text{Total mass} = \text{g/kg agent} * \text{lb agent} * .454 \text{ kg/lb}$$

$$= .022 * 130 * .454 = 1,300 \text{ g HCl}$$

E. VERTICAL PROFILE

1. Vertical profile (Sphere Canister) Volume Calculation

Follow the same protocol as for Summa® canisters to obtain volumes corrected to STP.

2. Sample Concentration Calculations

Injections were repeated until peak areas (from computerized integration) were within $\pm 10\%$.

The average was then taken of these readings, and divided by the daily response factor to give actual concentration.

The average daily response factor (RF) was calculated using the average of initial and final check standards injected for each run.

For run No. 6 (PFH), a 100 ppm standard was run:

	PFHa (initial)	PFHb (final)
Integrated areas:	1555328	1507776
	1550886	1505013
	+ 1558600	+ 1515676.7
	<hr/> 4664814	<hr/> 4528465.7
	÷ 3	÷ 3
	<hr/> 1554938	<hr/> 1509489

$$\text{Average Daily RF} = \frac{1554938 + 1509489}{2} = \frac{1532214}{100 \text{ ppm}} = 15322$$

from Sample 6014	185849.7
6014a	185571.7
	+ 190926.1
	<hr/> 562347.5
	÷ 3
	<hr/> 187449 = Average integrated area

$$\text{concentration (ppm)} = \frac{\text{Average integrated area}}{\text{RF}}$$

$$= \frac{187449}{15322} = 12 \text{ ppm}$$

F. DRAEGER TUBES

$$\text{Concentration (ppm v/v)} = \frac{\mu\text{HF} * 1000 * 29.92 * T}{\text{Flow} * \text{Burn time} * P * 535}$$

where:

- μHF = Draeger tube reading
- 29.92 = Standard pressure (inches Hg)
- T = Temperature (R)
- Flow = Burn time flow rate (cc/min)
- Burn time = Minutes
- P = Pressure (inches Hg)
- 535 = Standard temperature (R)

For Test 5, 45 degrees north of DN CL inner screen pump No. 2168

- Draeger reading = 25
- Temperature = 528R
- Flow = 99 cc/min
- Burn time = 35 sec
- Pressure = 24.65 inches Hg

$$\frac{25 * 1000 * 29.92 * 528}{99 * \left(\frac{35}{60}\right) * 24.65 * 535} = 518 \text{ HF Equivalents}$$

from FTIR analysis of Run 5

HF	=	119.51	}	Multiply by RF
HCl	=	239.54		
COF ₂	=	72.12		

*	1	=	119.51	}	Adjusted Concentration
*	1.5	=	359.01		
*	0.2	=	14.42		
<hr/>					
492.94				=	Total adjusted concentration

$$\text{Actual concentration} = \frac{\text{HF equiv. (Ratio of Adjusted conc)}}{\text{RF}}$$

$$\text{HF} = \frac{518 \left(\frac{119.51}{492.94} \right)}{1} = 126$$

$$\text{HCl} = \frac{518 \left(\frac{359.01}{492.94} \right)}{1.5} = 252$$

$$\text{COF}_2 = \frac{518 \left(\frac{14.42}{492.94} \right)}{0.2} = 76$$

$$\text{IDLH} = \frac{\text{Actual conc}}{\text{IDLH value}}$$

$$\text{HF} = \frac{126}{30} = 4.2 \quad \text{HCl} = \frac{252}{100} = 2.52 \quad \text{COF}_2 = \frac{76}{15} = 5.1$$

G. FIREFIGHTER EXPOSURE MODELING

1. FTIR Fire Phase

$$\text{Total acid gas exposure} = \frac{\text{conc HCl}}{\text{HCl IDLH}} + \frac{\text{conc HBr}}{\text{HBr IDLH}} + \frac{\text{conc HF}}{\text{HF IDLH}} + \frac{\text{conc COF}_2}{\text{COF}_2 \text{ IDLH}}$$

(example—Run 5)

$$\text{Total acid gas} = \frac{240}{100} + \frac{0}{50} + \frac{120}{30} + \frac{72}{15} = 11.2$$

2. Emission Rates (for FTIR)

$$\frac{(\text{Acid gas ppm} * \text{Acid gas M.W.})}{(\text{Agent ppm} * \text{Agent M.W.})} * \text{Agent integrated flow rate}$$

(example HCl emission rate—Run 2)

$$\frac{(80 \text{ ppm} * 36.4 [\text{M.W. HCl}])}{(4300 \text{ ppm} * 165.5 [\text{M.W. Agent}])} * 1.25 \text{ lb/sec} * 454 \text{ g/lb} = 2.32 \text{ g/sec}$$

3. Concentrations

$$\frac{(\text{Emission rate of compound}) * (\text{Maximum modeled conc. at receptor location})}{(\text{Unit emission rate}) * 1000}$$

(amount is divided by 1000 converting micrograms to milligrams)

(Example Run 2—HCl at 5 meters)

$$\frac{2.32 \text{ g/s}}{1 \text{ g/s}} * \frac{236587 \text{ } \mu\text{g/m}^3}{1000 \text{ } \mu\text{g/mg}} = 549 \text{ mg/m}^3$$

4. IDLH Level Calculations

$$(\text{IDLH value (ppm)}) * \frac{1}{24.5 \text{ L/mole}} * (\text{gram molecular weight})$$

(example HCl)

$$100 \text{ ppm} * \frac{1}{24.5 \text{ L/mole}} * 36.5 = 150 \text{ mg/m}^3$$

$$\frac{(\text{Scaled target conc})}{(\text{IDLH value})}$$

(example HCl Run 2)

$$\frac{549 \text{ mg/m}^3}{150 \text{ mg/m}^3} = 3.66 \text{ (multiple of IDLH level)}$$

5. PEL Levels

$$\frac{(\text{Scaled target conc})}{(\text{PEL value})}$$

$$\frac{549 \text{ mg/m}^3}{7.5 \text{ mg/m}^3} = 7.32 \text{ multiples of PEL level}$$

H. COMMUNITY EXPOSURE

- * 100-pound agent
- * emission spread over 15 minutes

$$= 454 \text{ g/lb} * 100 \text{ lb} = 45400 \text{ g}$$

$$45400 \text{ g} * \frac{1}{15 \text{ min}} * \frac{1 \text{ min}}{60 \text{ sec}} = 50.44 \text{ g/sec}$$

- * Ratio method emission rate

example HCl run 2

$$\frac{80 \text{ ppm} * 36.5 \text{ MW HCl}}{4300 \text{ ppm} * 165.5 \text{ MW agent}} * 50.44 \text{ g/sec} = 0.21 \text{ g/sec}$$

- * Note the runs considered are Run 2 Halon 1211, Run 5 HCFC 123, and Run 8 PFH.

Resulting emission rates g/sec				
	HCl	HF	HBr	COF ₂
H1211	0.21	0.066	0.91	0.17
123	1.2	0.33	—	0.47
PFH	—	0.26	—	0.91

Method 2 Calculation Scheme

Step 1 Molecular Weight of Plume

Plume =	86.5	moles N ₂	MW = 28
	11	moles CO ₂	= 44
	12	moles H ₂ O	= 18
	<u>109.5</u>	moles in Plume	

avg molecular weight of plume

N ₂	CO ₂	H ₂ O
$\frac{86.5}{109.5} \times 28$	$+ \frac{11}{109.5} \times 44$	$+ \frac{12}{109.5} \times 18$
$= 28.54 \text{ avg molecular weight of plume}$		

Step 2 Plume Volume due to JP-4 Combustion

Example Calculation from Run 1

Air Fuel Ratio = 20 19 moles air: 1 mole JP-4 (20 moles total)

Fuel Used = 20 gal

Time of fire duration = 4.5 min

$$20 \text{ gal} * 3.785 \text{ L/gal} * .741 \text{ kg/L} * 20 * \frac{1}{4.5 \text{ min}}$$

$$= 249.31 \text{ kg/min} * \frac{1 \text{ kmole}}{28.54 \text{ kg}}$$

$$= 8.74 \text{ kmole/min} * 24.5 \text{ m}^3/\text{kmole}$$

$$= 214.02 \text{ m}^3/\text{min} = 214 \text{ m}^3/\text{min}$$

FTIR Acid Gas Emission Rates Based on Volume

$$\left(\frac{\text{Agent amt lb}}{\text{Fire length minutes}} \times \frac{1 \text{ kg}}{2.2 \text{ lb}} \times 24.5 \text{ L/mole} * \frac{1 \text{ mole}}{\text{Halon MW g}} \right) = \frac{\text{m}^3}{\text{min}}$$

Example Run 2

$$\frac{150 \text{ lb}}{2 \text{ min}} \times \frac{1 \text{ kg}}{2.2 \text{ lb}} * \frac{24.5 \text{ m}^3}{\text{kmole}} \times \frac{1 \text{ kmole}}{16.55 \text{ kg}} = \frac{5.05 \text{ m}^3}{\text{min}} \text{ agent volume}$$

Run 2 HCl example calculation 80 ppm detected in plume

$$80 \text{ ppm HCl} * \frac{35.4 \text{ g/mole HCl}}{24.5 \text{ L/mole}} = 115.6 \text{ mg/m}^3 \text{ HCl} \rightarrow$$

Agent Emission Rate

$$A = 115.6 \text{ mg/m}^3 * 5.05 \text{ m}^3/\text{min} = 584 \text{ mg/min}$$

Plume Emission Rate

$$B = 115.6 \text{ mg/m}^3 * 214 \text{ m}^3/\text{min} = 24,738 \text{ mg/min}$$

$$\text{Then } A + B = 584 + 24,738 = 25,322 \text{ mg/min}$$

$$25,322 \text{ mg/min} \times 1/1000 \text{ g} \times 1 \text{ min}/60 \text{ sec} = 0.41 \text{ or } 0.42 \text{ g/sec rounding}$$

8/24-hour emissions (g/sec)

Agent		HCl	HF	HBr	COF ₂
H1211	Run 2	0.41	0.13	1.8	0.33
H1211	Run 3	0.20	0.09	0.66	0.4
123	Run 4	2.4	0.65	—	0.94
123	Run 5	0.70	0.19	—	0.37
PFH	Run 7	—	0.41	—	1.8
PFH	Run 8	—	0.51	—	1.3
PFH	Run 9	—	0.50	—	0.80
123	Run 10	0.49	0.17	—	0.26

For any compound at 1 g/sec unit emission rate:

8-hour concentration highest $\mu\text{g}/\text{m}^3$

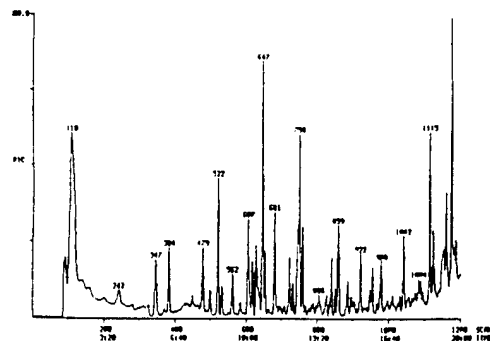
Range	100	200	300	400	500	600	700	800	900	1
Concentration	669	183	84	48	30	21	15	12	9.3	7.5
24-hour										
Concentration	321	91	37	20	17	9	6	5	3	2

APPENDIX C
MAIN STUDY DATA

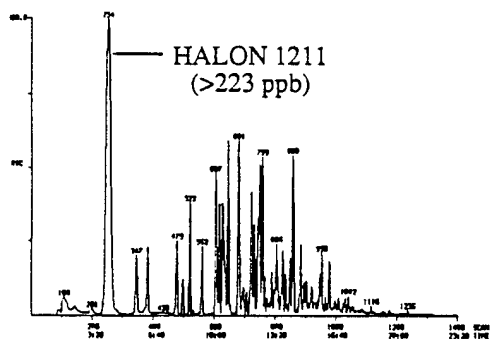
TABLE C-1. METHOD DETECTION LIMITS AND CONCENTRATION RANGES FOR MAIN TEST VOCs.

Analyte	Tenax®/charcoal absorbent trap (ppb)		Summa® cannister 1-L analysis volume (ppb)		Summa® cannister 5-µL analysis volume (ppb)	
	Min	Max	Min	Max	Min	Max
Halon 1211	0.26	32	6.0	730		150,000
HCFC 123	0.21	26	4.8	600		123,000
Perfluorohexane	0.10	12	2.2	270		55,000
Dichlorodifluoromethane	0.27	33	6.0	760		155,000
Chloromethane	0.64	80	14.7	1,830		370,000
1,3-Butadiene	0.60	74	13.6	1,700		350,000
Dichlorofluoromethane	0.32	39	7.2	900		183,000
1,2-Dichloro-1,1,2-trifluoroethane	0.21	26	4.8	600		123,000
Dibromofluoromethane	0.17	21	3.8	480		97,000
Benzene	0.41	51	9.4	1,170		240,000
Dibromomethane	0.18	23	4.2	530		108,000
Toluene	0.35	44	8.0	1,000		203,000
<i>m</i> -and <i>p</i> -xylene	0.30	38	6.9	860		177,000
Ethynylbenzene	0.32	39	7.2	900		183,000
<i>o</i> -Xylene	0.30	38	6.9	860		177,000
Styrene	0.31	39	7.0	880		180,000
1-Phenyl-1-propyne	0.28	35	6.3	790		161,000
4-Ethynyltoluene	0.28	35	6.3	790		161,000

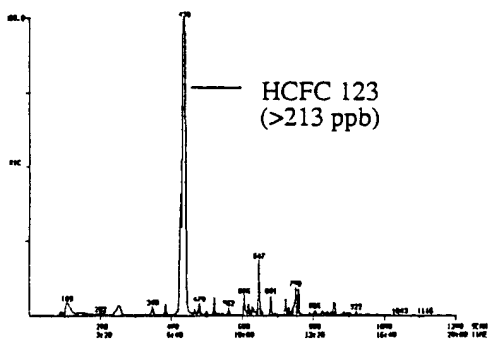
FF VOC's T/C



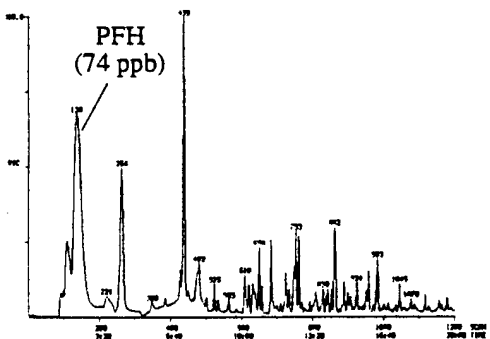
JP4



JP4 + 1211



JP4 + 123



JP4 + PFH

Figure C-1. Example RICs (Reconstructed Ion Chromatogram) for Tenax[®]/charcoal absorbent traps collected in the firefighter's breathing zone.

TABLE C-2. SUMMARY OF TICs (TENTATIVELY IDENTIFIED COMPOUNDS) IN
THE FIREFIGHTER'S BREATHING ZONE FOR MAIN TEST
(Concentration ppb).

Sample No.:	1013	2013	3013	5013
Agent used:	none	Halon 1211	HCFC 123	PFH
Compound				
Methylcyclopentane	24	-	-	-
Dimethylcyclopentane	10	-	-	-
Methylcyclohexane	74	-	-	-
Ethylbenzene	-	4	-	0.3
Dimethylbenzene	-	-	10	-
Ethylmethylbenzene	-	8	-	-
Trimethylbenzene	-	2	-	-
Methylpropylbenzene	-	1	-	-
Methylphenylethane	-	1	-	-
Carbon dioxide	34	-	-	-
2-Methylfuran	-	1	-	1
Trimethylmethoxysilane	-	-	-	3

TABLE C-3. SUMMARY OF PLUME SAMPLE TICs FOR THE MAIN TEST.

Compound	Concentration (ppb)				
	Agent:	None	Halon 1211	HCFC 123	Perfluorohexyl
	Sample No.:	1012	2012	3012	5012
Methylcyclopentane		1	15	17	2
Dimethylcyclopentane			8	6	
Methylcyclohexane			50	50	5
Dimethylcyclohexane			5		
Ethylcyclohexane			16	17	2
Trimethylcyclohexane				5	0.6
Trimethylcyclopentane				3	1
Dimethylhexane				5	
Ethylbenzene		0.5	12	3	0.6
Ethylmethylbenzene			2	2	
Methylethylbenzene			3	2	
2-Hexane		3			
Chlorotrifluoromethane				65	
Trifluorochloroethane				16	
Difluorodichloroethane				4	
Hydroxypropanone				21	
Trifluorodichloropropene				1	
Trichlorofluoroethene				3	
Chloromethyl methoxybenzene				2	
Methylheptane				3	
Methylethylcyclohexane			4	6	0.8
Methylpropylbenzene				1	
Hexafluoroethane					21
Tetradecafluorohexane					4
Dimethyltricyclohexane					0.2
Pentylcyclohexane					0.7
Dimethylcyclopropane		0.8			
Methylbutanone		14			
Trichloroeicosysilane		1			
Butanoic acid		1			
Octamethylcyclotetrasilane		3			
Epoxyethylbutanone		4			
Phenylethanone		1			
Nonanone		6			
Chlorodifluoromethane			5		
Bromopropene			2		
Bromochloromethane			2		

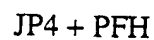
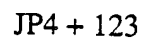
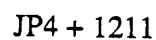


Figure C-2. Example RICs for Summa® canister samples collected in the plume.

TABLE C-4. SUMMARY OF DOWNWIND LOCATION TICs FOR THE MAIN TEST.

Compound	Concentration (ppb)				
	Agent:	None	Halon 1211	HCFC 123	Perfluorohexyl
	Sample No.:	1027	2027	3027	5027
Methylcyclopentane			20	20	2
Dimethylcyclopentane					2
Methylcyclohexane			78	75	9
Dimethylcyclohexane			26		0.4
Ethylbenzene				7	0.7
Ethylmethylbenzene				6	0.3
Methylethylbenzene				1	
Butanone					
Methylfuran		2			
Hexane			23		
Carbon dioxide			15		
Methylheptanone		16			
Hexanone		4			
Trichlorotrifluoroethane		12			
Dibromochlorofluorocyclopropane		58			
Dichlorotrifluoroethane			2		
Methylpentane			19		
Trimethylpentane			9		
Dimethylhexane			14		
Tetradecafluorohexane					8
S-Methyloctane					1
Dimethoxymethane					0.2
Ethylmethylbenzene				2	
Methylpropylbenzene				3	
Trimethylbenzene				2	
Butylcyclohexane				8	
Ethylcyclohexane				20	
Trimethylcyclopentane				6	
Butanone				3	
Dichloromethane				35	
Dichloropentafluorobutane				5	
Dichlorotetrafluoroethane				7	
Dimethyltricyclopentane				10	
Dimethyltricyclohexane				6	
Dimethyl- <i>cis</i> -cyclohexane				3	

PLUME VOC's T/C

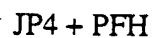
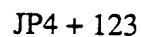
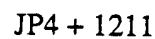


Figure C-3. Example RICs for Tenax®/charcoal adsorbent traps collected in the plume.

TABLE C-5. PARTICULATE RESULTS.

Filter number	Sample position	Tare 1 (mg)	Tare 2 (mg)	Avg. tare (mg)	Final wt. (mg)	Weight diff. (mg)	Rinse wt. (mg)	Total mass (mg)
1	SW, Run 1	715.20	715.30	715.250	715.60	0.35		0.35
2	PL, Run 1	716.35	716.40	716.375	739.90	23.52	32.2	55.725
3	FF, Run 1	716.25	716.25	716.250	717.10	0.85		0.85
4	DW, Run 2	718.30	718.35	718.325	720.00	1.67		1.675
5	PL, Run 2	714.10	714.20	714.150	723.60	9.45	19.8	29.25
6	FF, Run 2	708.40	708.45	708.425	709.40	0.97		0.975
7	DW, Run 3	711.30	711.35	711.325	713.80	2.47		2.475
8	PL, Run 3	715.40	715.35	715.375	621.40	-93.98	49.9	-44.075
9	FF, Run 3	714.95	715.00	714.975	716.40	1.42		1.425
10	DW, Run 4	707.15	707.20	707.175	708.70	1.52		1.525
11	PL, Run 4	713.25	713.25	713.250	704.70	-8.55	11.9	3.35
12	FF, Run 4	711.25	711.30	711.275	712.20	0.93		0.925
13	DW, Run 5	715.50	715.55	715.525	718.50	2.98		2.975
14	PL, Run 5	721.30	721.30	721.300	638.00	-83.30	5.2	-78.1
15	FF, Run 5	715.40	715.45	715.425	716.70	1.27		1.275
16	DW, Run 6	719.45	719.60	719.525	713.90	-5.63		-5.625
17	PL, Run 6	722.30	722.35	722.325	676.60	-45.73	5.6	-40.125
18	FF, Run 6	718.65	718.60	718.625	719.80	1.17		1.175
19	Blank	718.85	718.90	718.875	719.40	0.52		0.525
20	Upwind	724.95	724.95	724.950	725.50	0.55		0.55

Concentration (mg/m³, std.)

Volumes

DW, Run 112-2 scf x (2.832 x 10⁻² m³/ft³)

PL, Run 147.3 scf

FF, Run 137.8 scf

1.01

41.6

0.79

TABLE C-6. SUMMARY OF TICs FOR FIREFIGHTER SVOs FOR MAIN TEST
(Runs 1 to 7; results reported in total $\mu\text{g}/\text{m}^3$)^a.

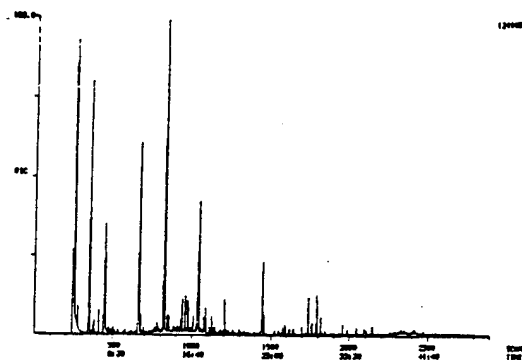
Compound	Run 1 Jet fuel C + F 1006-1007	Run 2 Halon 1211 C + F 2006-2007	Run 4 HCFC 123 C + F 3006-3007	Run 5 HCFC 123 C + F 4006-4007	Run 6 PFH C + F 5006-5007	Run 7 PFH C + F 6006-6007
Methyl benzenediamine	26			16		
Unknown carboxylic acid			4.7	17		
Unknown aromatic ester			42			
Unknown C11-C13 hydrocarbon						15
Lab code	27951	27953	27955	27957	27959	27961
GC/MS file (6207...)	K21W2	K21W4	K21W6	K21W7	K21W8	K22W4
Date sampled						
Date analyzed	Nov-21-91	Nov-21-91	Nov-21-91	Nov-21-91	Nov-21-91	Nov-22-91

^a Sample split factor = 2; final sample extract volume = 100 μl .
C = cartridge, F = filter, R = probe rinse.

Run # 1

JP4

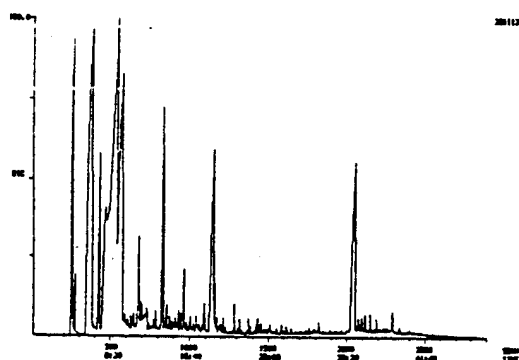
(a)



Run # 2

JP4 + 1211

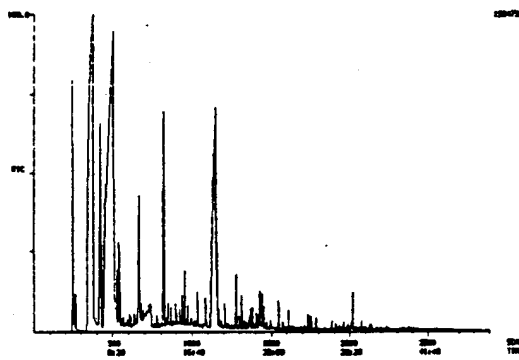
(b)



Run # 4

JP4 + 123

(c)



Run # 6

JP4 + PFH

(d)

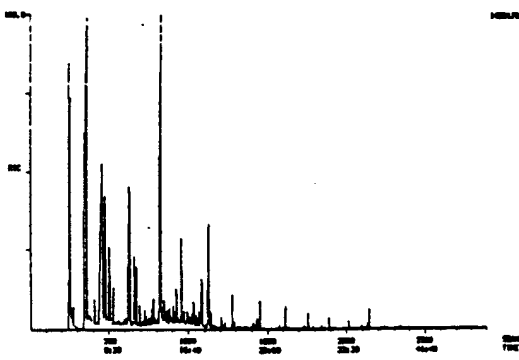


Figure C-4. Example RICs for PUF samples from plume—Main Test.

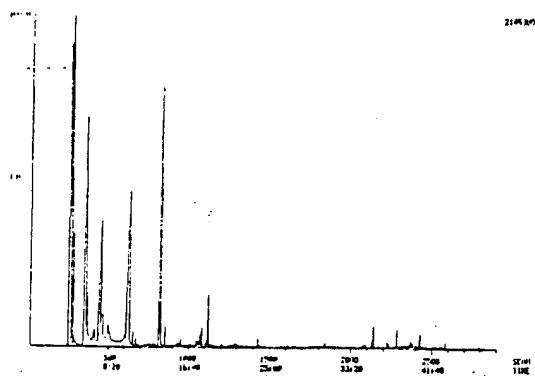
TABLE C-7. SUMMARY OF TICs FOR SVOs
ANALYSIS OF PLUME SAMPLES FOR MAIN TEST
(Runs 1 to 7; results reported in total $\mu\text{g}/\text{m}^3$)^a.

Compound	Run 1 Jet Fuel C + F + R 1003-1005	Run 2 Halon 1211 C + F + R 2003-2005	Run 4 HCFC 123 C + F + R 3003-3005	Run 5 HCFC 123 C + F + R 4003-4005	Run 6 PFH C + F + R 5003-5005	Run 7 PFH C + F + R 6003-6005
Chlorotoluene		280	940			27
Methylphenol		570	5400		100	74
Bromotoluene		980			11	
Unknown C10-C15 hydrocarbon	12	79	85		53	
Benzoic acid			210			
Benzothiozole					5.3	
Biphenylene	12					
Ethylhexyl propenoic acid	8					
Unknown substituted benzene			3000		22	
Unknown substituted cyclohexane					7.2	
Unknown carboxylic acid			170		27	
Unknown substituted chlorotoluene				46		
Unknown phthalate						51
Unknown		1500	78	58	16	30
Lab code	27963	27964	27965	27966	27967	27968
GC/MS file (6207...)	K22W12	K22W11	K22W10	K22W5	K22W7	K22W2
Date sampled						
Date analyzed	Nov-22-91	Nov-22-91	Nov-22-91	Nov-22-91	Nov-22-91	Nov-22-91

^a Sample split factor = 2; final sample extract volume = 100 μL .
C = cartridge, F = filter, R = probe rinse.

Run # 1

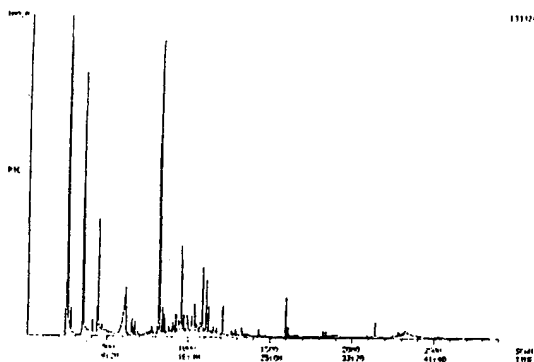
(a)



JP4

Run # 2

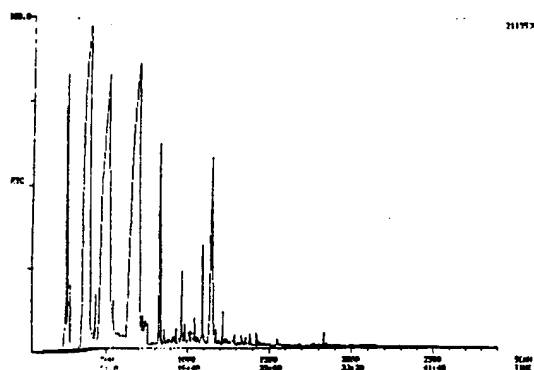
(b)



JP4 + 1211

Run # 4

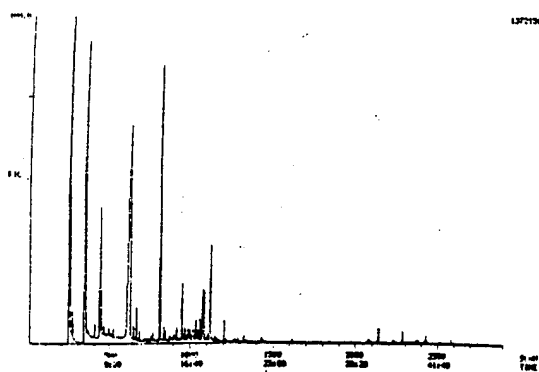
(c)



JP4 + 123

Run # 6

(d)



JP4 + PFH

Figure C-5. Example RICs for downwind samples for Main Test.

TABLE C-8. SEMIVOLATILE TENTATIVELY IDENTIFIED COMPOUNDS (TICs)
OBSERVED FOR THE DOWNWIND
(Runs 1 to 7; results reported in total $\mu\text{g}/\text{m}^3$)^a.

Compound	RUN 1 JET FUEL C + F + R 1024-1025	RUN 2 HALON 1211 C + F + R 2024-2025	RUN 4 HCFC 123 C + F + R 3024-3025	RUN 5 HCFC 123 C + F + R 4024-4025	RUN 6 PFH C + F + R 5024-5025	RUN 7 PFH C + F + R 6024-6025
Benzoyl chloride			1900			
Methyl phenol	140		13			450
Substituted chlorobenzene			21			
Unknown C6-C15 hydrocarbon		86	840	57	51	170
Benzoic Acid			32			
Unknown substituted benzene		32	420			19
Unknown phthalate	100				49	
BHT (butylated hydroxytoluene)		36				
Unknown C8H16 subcyclohexane						49
Dimethylnaphthalene						23
Unknown	39					
Lab code	27952	27954	27956	27958	27960	27962
GC/MS file (6207...)	K21W3	K21W5	K22W6	K22W8	K22W3	K22W9
Date sampled						
Date analyzed	21 Nov 91	21 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91	22 Nov 91

^a Sample split factor = 2, final sample extract volume = 100 μl .
C = cartridge, F = filter, R = probe rinse.

FTIR DATA

Test #1

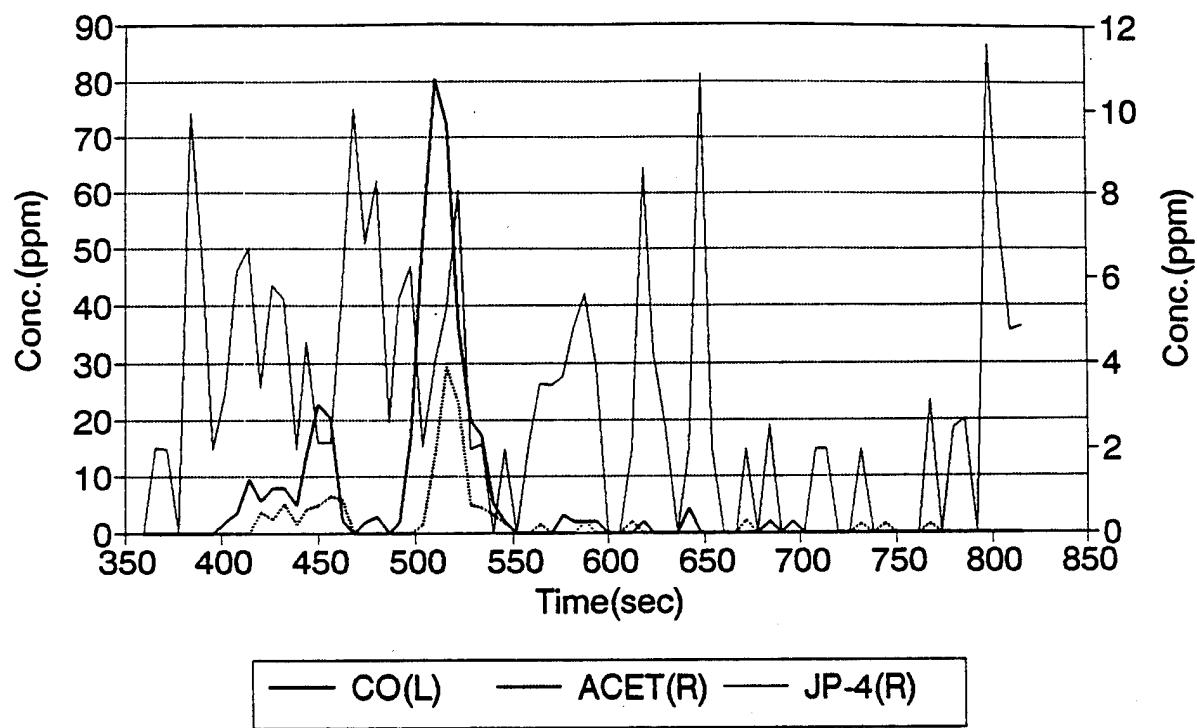


Figure C-6. Concentration plots for Test 1—fire only.

FTIR DATA

Test #2

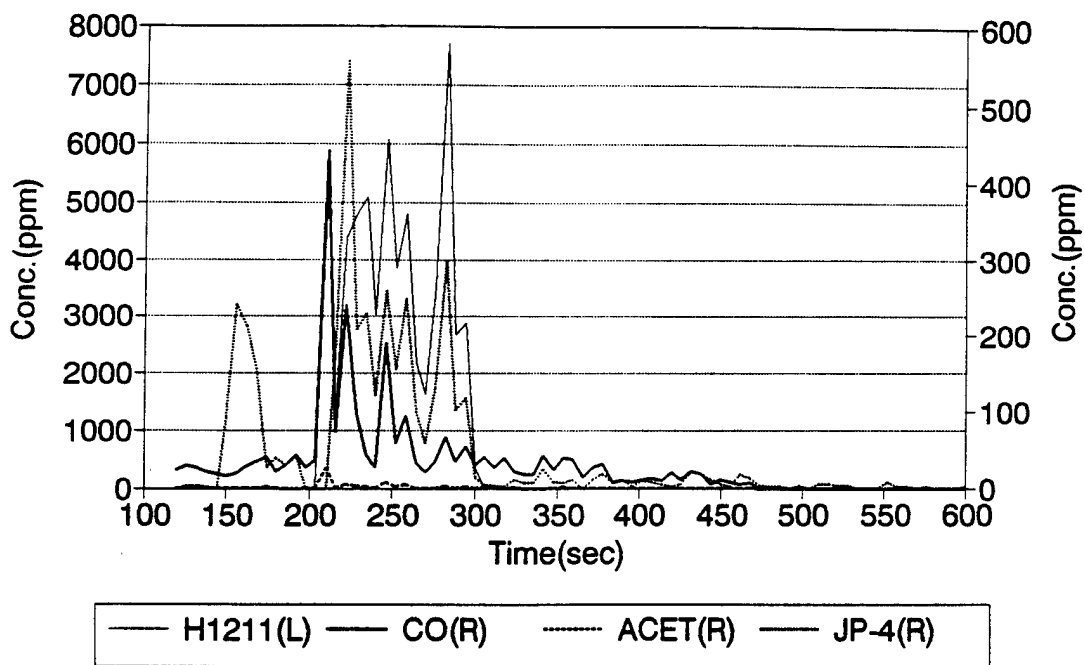
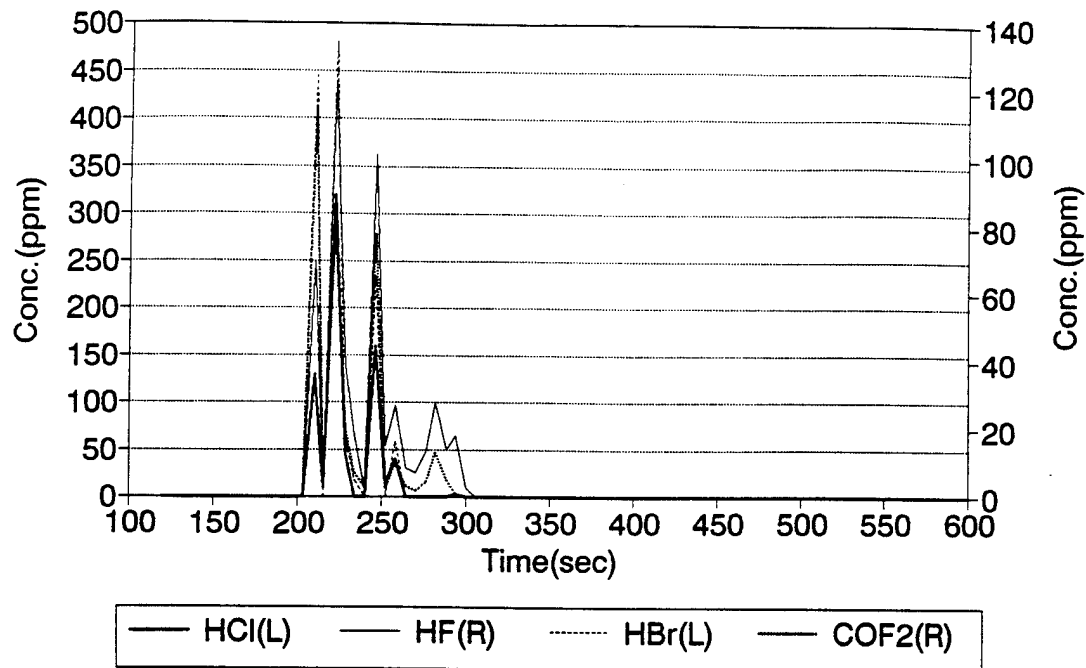


Figure C-7. Concentration plots for Test 2—Halon 1211—fire not extinguished.

FTIR DATA

Test #3

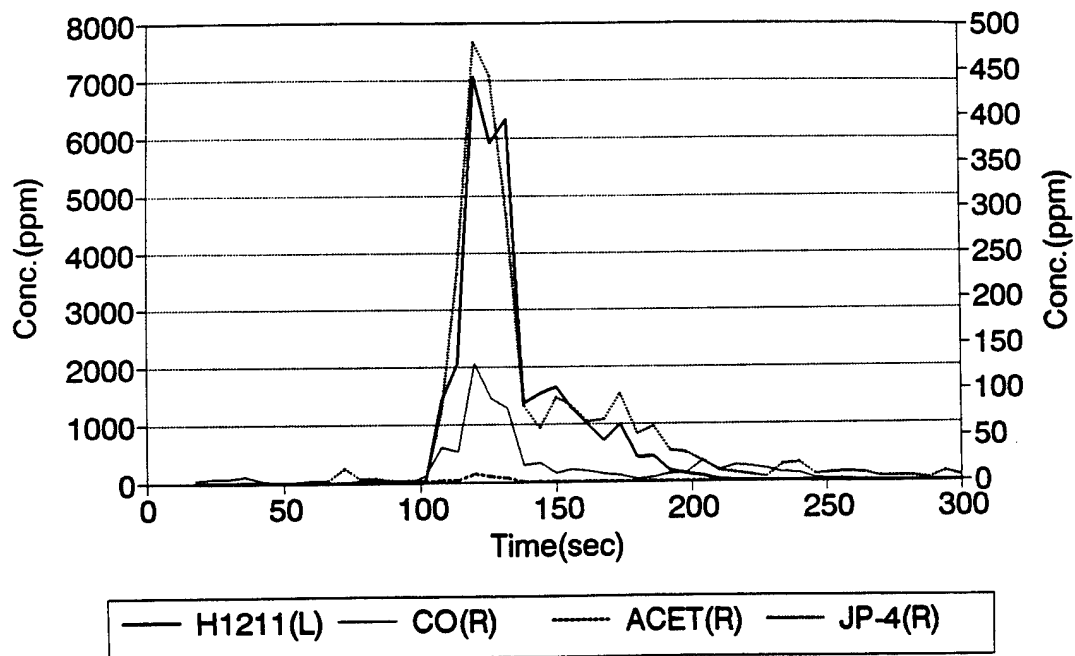
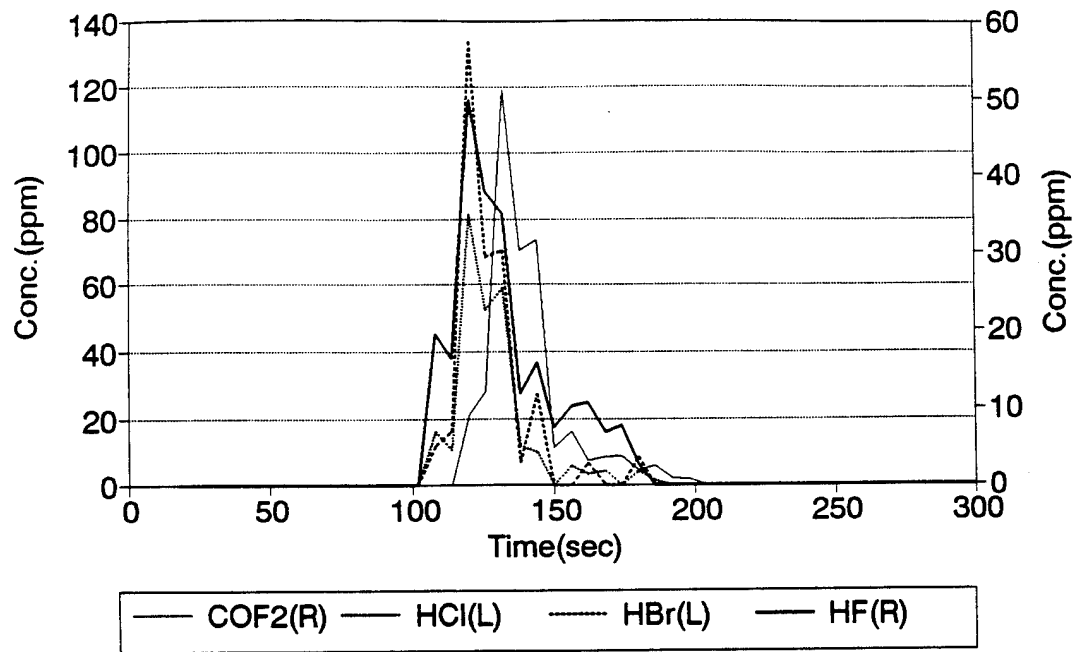


Figure C-8. Concentration plots for Test 3—Halon 1211—long path.

FTIR DATA

Test #4

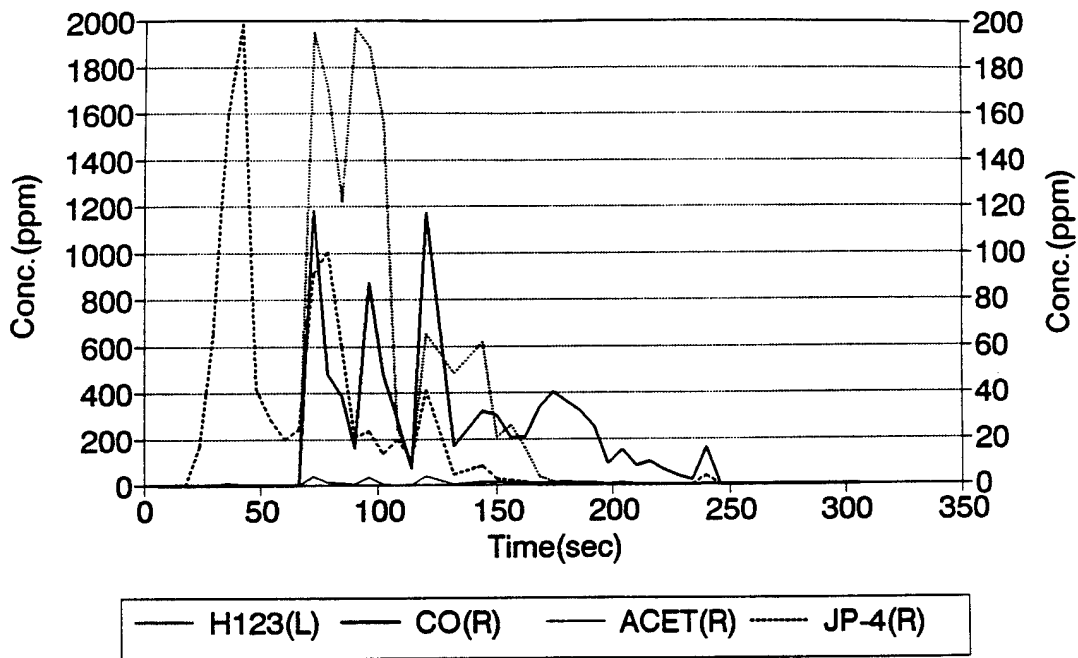
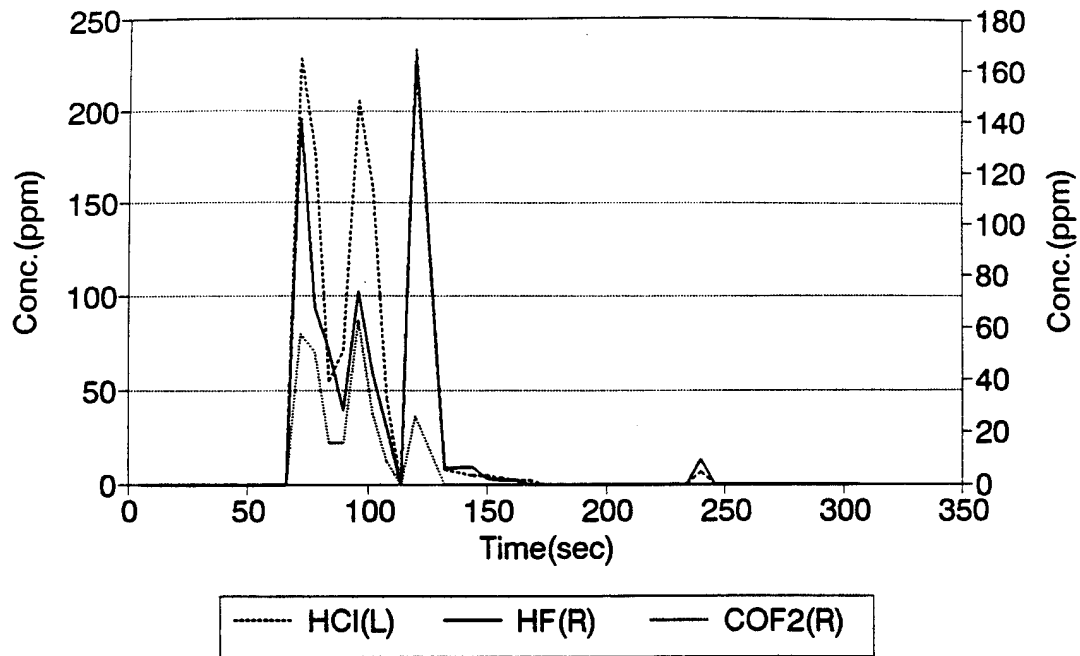


Figure C-9. Concentration plots for Test 4—HCFC 123—fire not extinguished.

FTIR DATA

Test #5

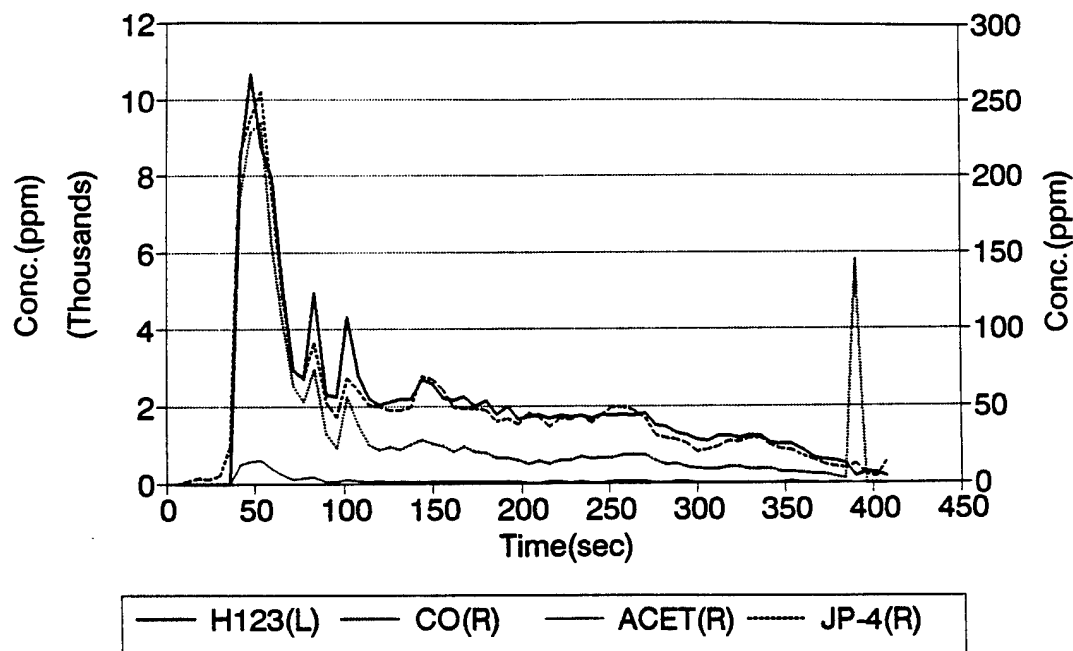
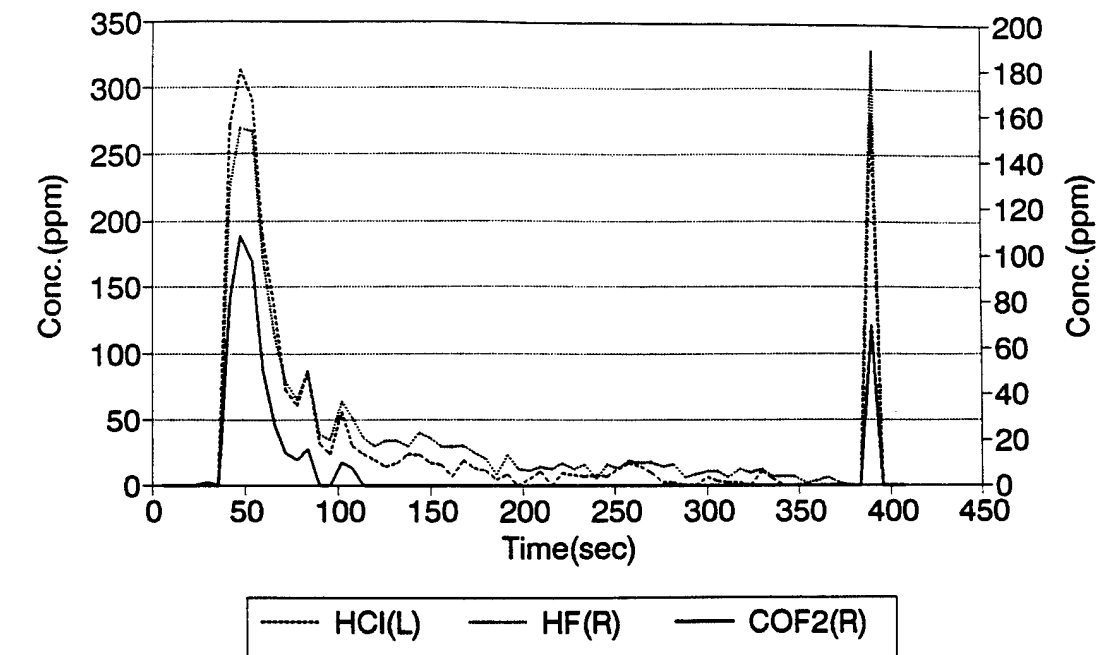


Figure C-10. Concentration plots for Test 5—HCFC 123.

FTIR DATA

Test #7

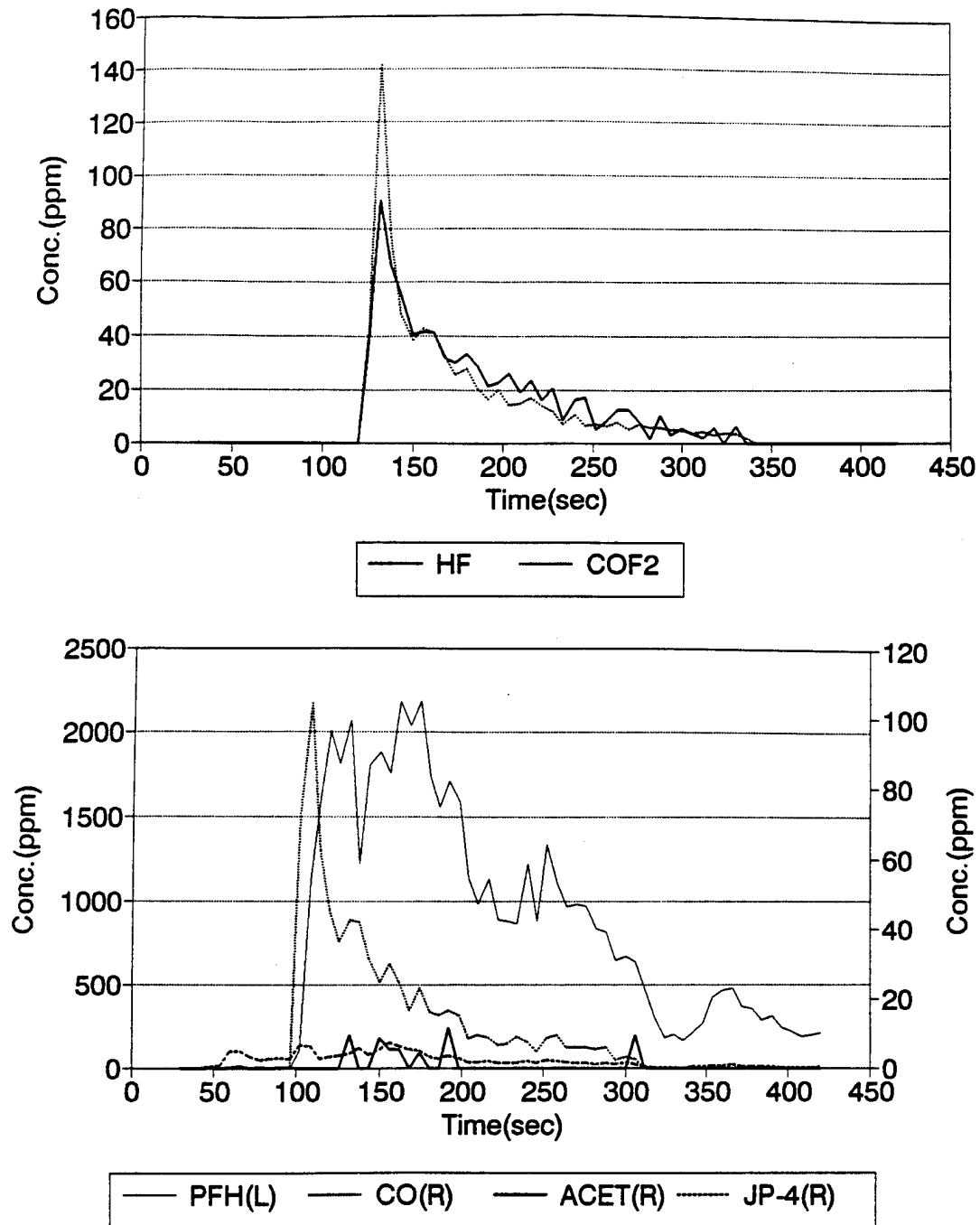


Figure C-11. Concentration plots for Test 7—perfluorohexane.

FTIR DATA

Test #8

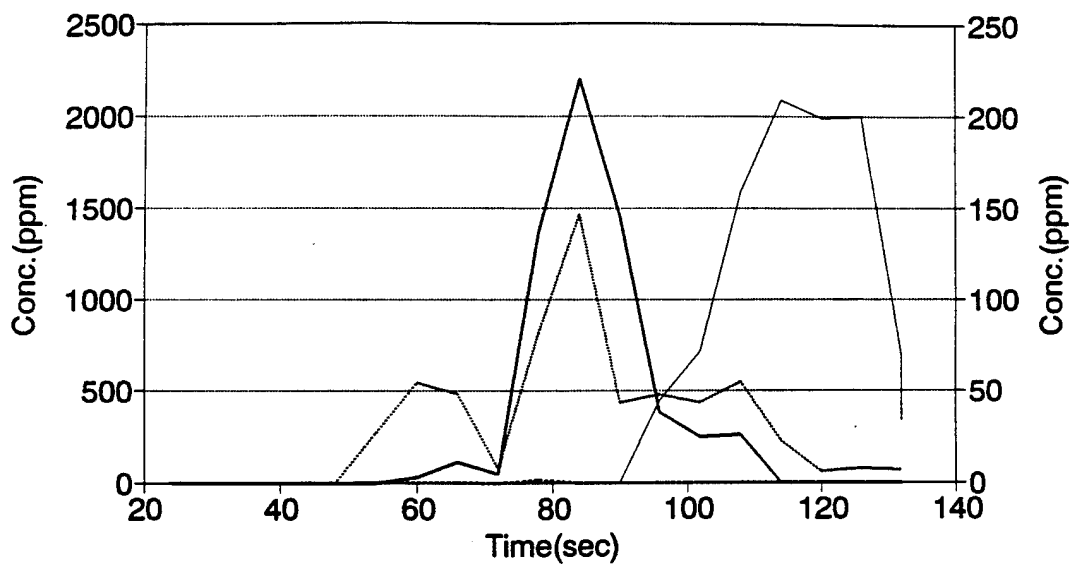
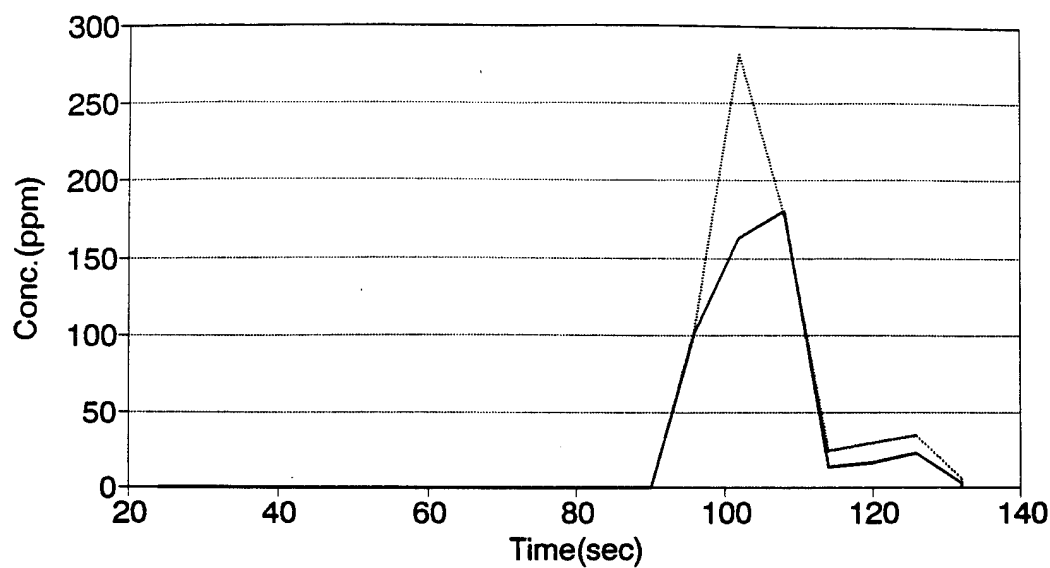


Figure C-12. Concentration plots for Test 8—perfluorohexane.

FTIR DATA

Test #9

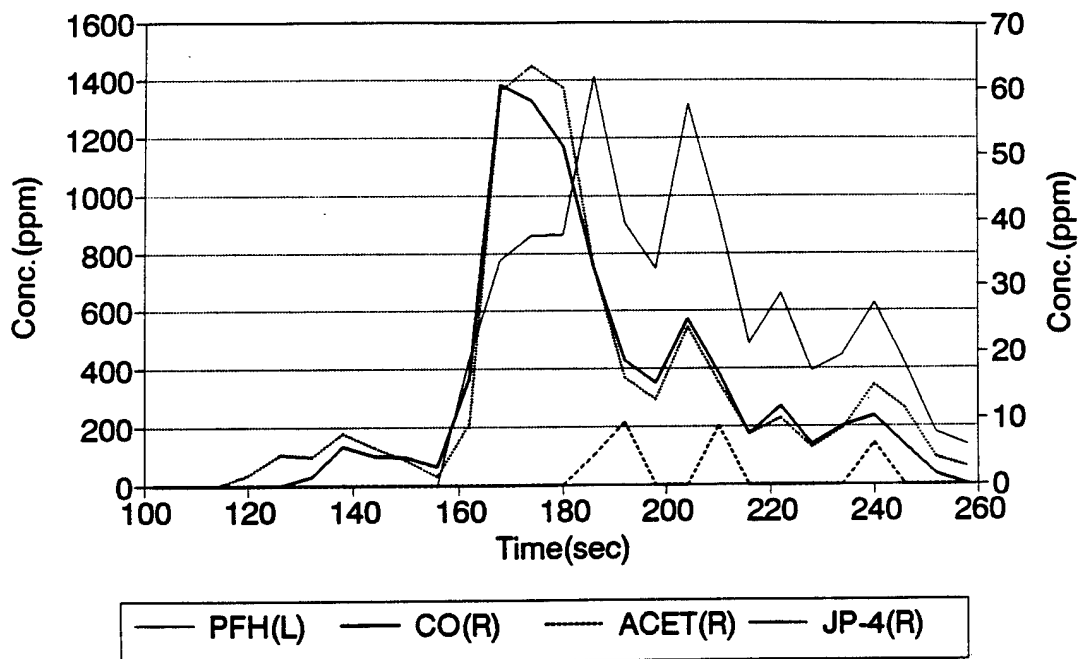
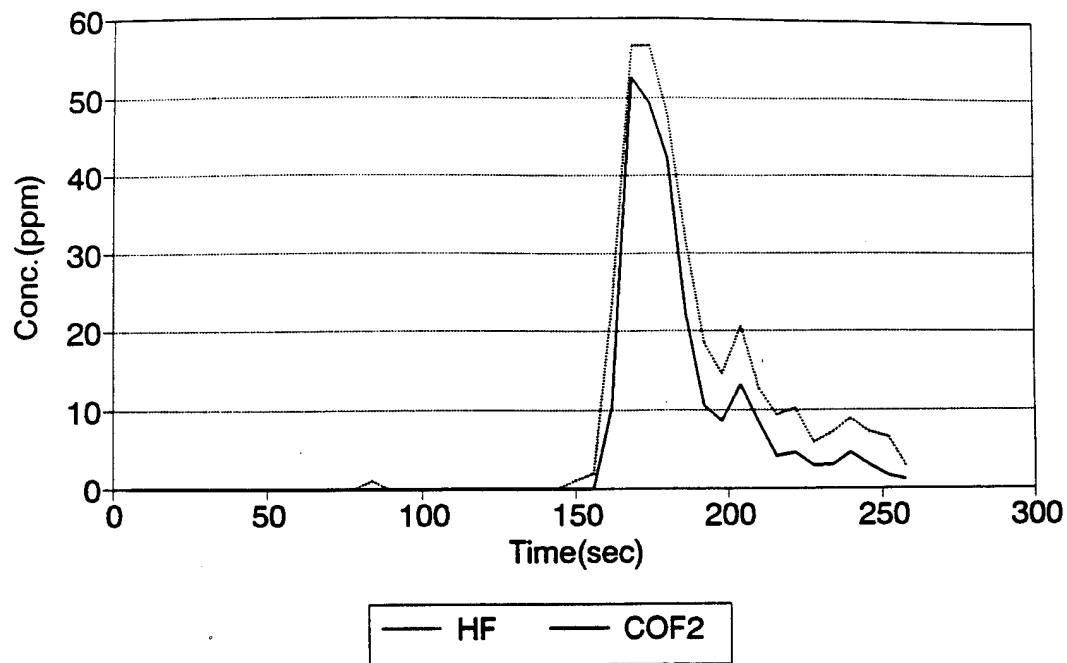
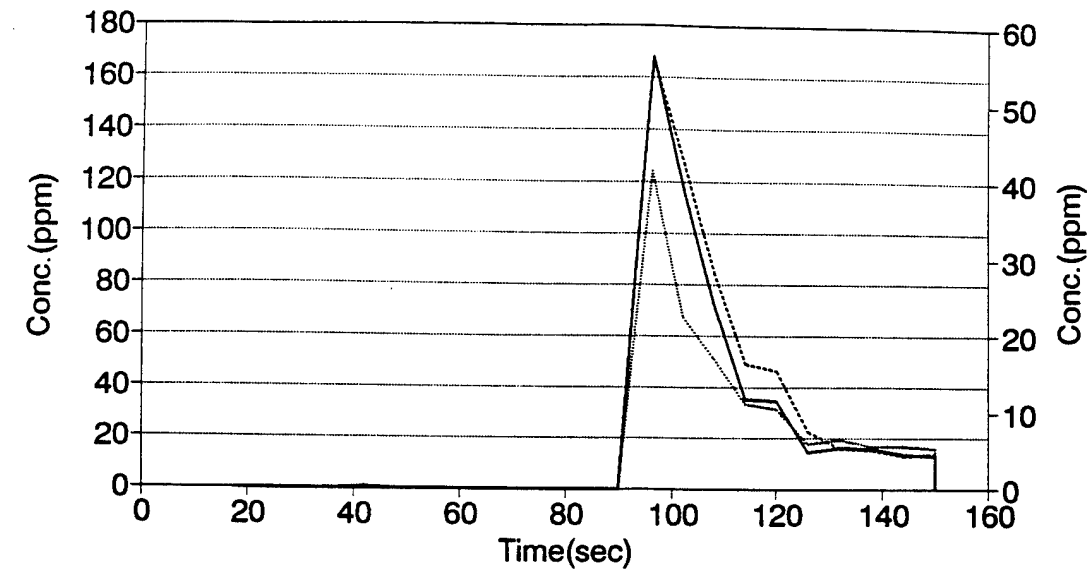


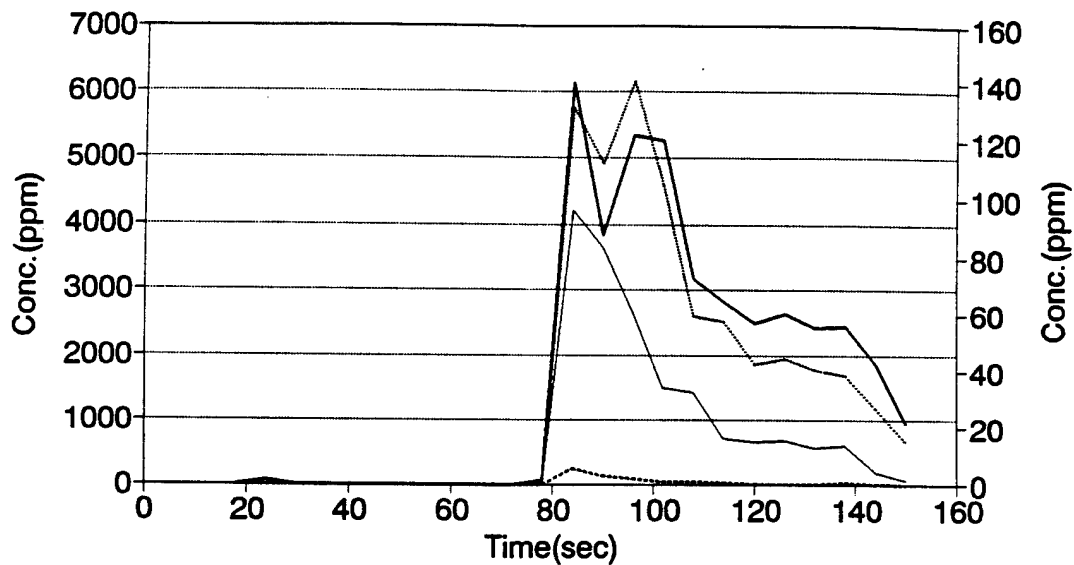
Figure C-13. Concentration plots for Test 9—perfluorohexane—long path.

FTIR DATA

Run #10



— HCl(L) — HF(L) — COF2(R)



— H123(L) — CO(R) — ACET(R) — JP-4(R)

Figure C-14. Concentration plots for Test 10—HCFC 123—long path.